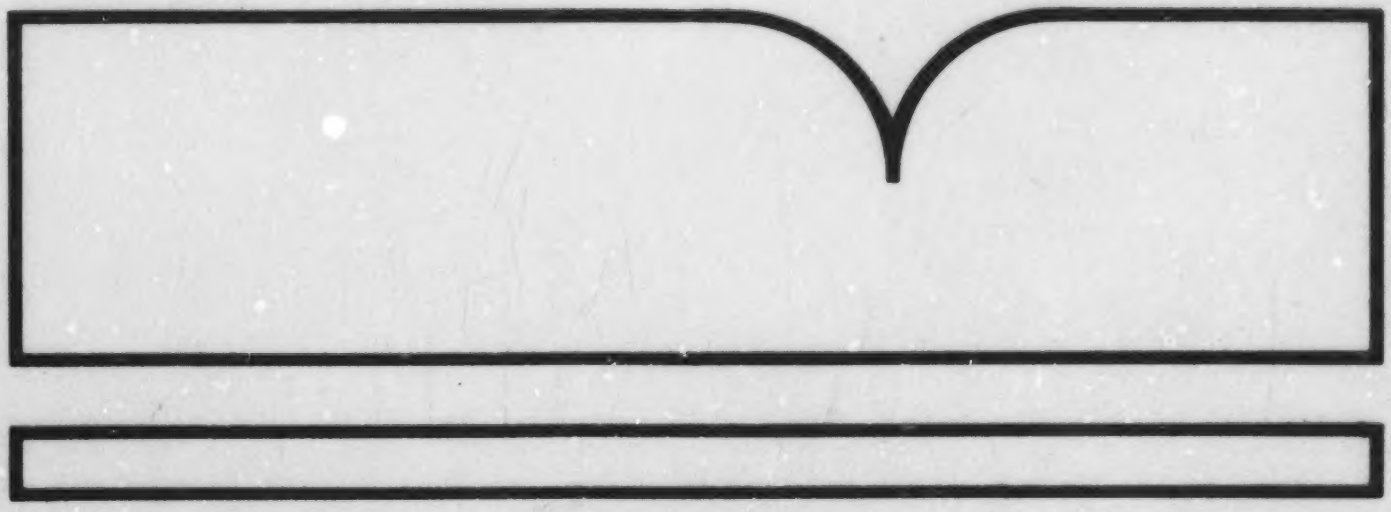
PB84-170984

Measurements of the Products of Atmospheric Photochemical Reactions in Laboratory Studies and in Ambient Air-Relationships Between Ozone and Other Products

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

1983



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1. REPORT NO. EPA-600/J-83-164	2.	3. R PB84-170984
4. TITLE AND SUBTITLE Measurements of the Products of Atmospheric Photochemical Reactions in Laboratory Studies and in Ambient Air-Relationships Between Ozone and Other Products		5. REPORT DATE 1983 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) (Journal Version) A. P. Altshuller		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS (Same as Block 12)		10. PROGRAM ELEMENT NO. CDWA1A/01-1642 (FY 82) 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES
REF: Atmospheric Environment, 17(12):2383-2427, 1983

16. ABSTRACT

Many inorganic and organic gaseous and aerosol products are formed in the atmosphere from atmospheric photochemical reactions. The mechanisms of formation, types of products identified, smog chamber studies, and ambient air concentrations and distributions are considered in this review. Because ozone is a key product which is widely measured, it is of considerable interest to determine whether the atmospheric distributions of the other products are strongly related to that of ozone.

The same products predicted by laboratory studies are present in significant concentrations in the atmosphere. None of these products, except nitrogen dioxide, are present at concentrations approaching that of ozone. In combination, the concentration of other products, even excluding nitrogen dioxide, can approach and sometimes exceed the concentrations of ozone. This is particularly so on a 24-hour average basis. The substantial ambient air concentration levels of combinations of other products is of possible concern from the air quality viewpoint.

The ambient air measurement results indicate that ozone cannot be expected to serve as an adequate surrogate for the other products. The laboratory studies relating the yields of ozone and other products to initial hydrocarbon and nitrogen oxide concentration and hydrocarbon composition also indicate that the variations in other products do not closely match those of ozone.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 46 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITIO

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EPA-600/J-83-164
JOURNAL ARTICLE

Atmospheric Environment Vol. 17, No. 12, pp. 2383–2427, 1983
Printed in Great Britain.

0004–6981/83 $3.00 + 0.00
Pergamon Press Ltd.

MEASUREMENTS OF THE PRODUCTS OF ATMOSPHERIC PHOTOCHEMICAL REACTIONS IN LABORATORY STUDIES AND IN AMBIENT AIR-RELATIONSHIPS BETWEEN OZONE AND OTHER PRODUCTS

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(*First received* 6 *October* 1982; *in revised form* 12 *April* 1983 *and received for publication* 23 *May* 1983)

Abstract—Many inorganic and organic gaseous and aerosol products including but not limited to aldehydes and ketones, CO, formic acid, peroxyacyl nitrates (PANs), nitric acid and other nitrates, sulfates and organic particles are formed in the atmosphere from atmospheric photochemical reactions. The types of products identified, relationships of products to reactants from smog chamber studies, and ambient air concentrations and distributions are considered in this review. Because O_3 is a key product which is widely measured, it is of considerable interest to determine whether the atmospheric distribution of the other products are strongly related to that of O_3.

Most of the same products observed in laboratory studies are present at significant concentrations in the atmosphere. Concentrations of these products usually are at their highest levels in the South Coast Air Basin of California. However, the concentrations of products at other urban locations in the United States do overlap those at locations within the South Coast Air Basin. Peroxyacetyl nitrate (PAN) has been measured in London and Tokyo at concentrations in the same range as in cities within the United States. At nonurban sites the concentrations of the products measured are significantly lower than in urban locations. In clean maritime air the concentrations of several products have been reported to be between 1 and 10% of the concentrations in urban areas.

None of the other products are present individually at concentrations approaching that of O_3. In combination, the concentration of other products, even excluding NO_2, in some urban locations can approach and sometimes exceed the concentrations of O_3, especially on a 24-h average basis. The substantial ambient air concentration levels of combinations of products other than O_3 and NO_2 are of possible concern from the air quality viewpoint.

The ambient air measurements indicate that O_3 may serve directionally, but cannot be expected to serve quantitatively as an surrogate for the other products. The laboratory studies relating the yields of O_3 and other products to initial hydrocarbon (HC) and NO_2 concentration and HC composition indicate that the variations in other products do not closely match those of O_3.

1. INTRODUCTION

During the last 25 years much concern and effort has been directed at reducing the concentration levels of oxidants and particularly of O_3 in the lower atmosphere. O_3 has been identified as a key atmospheric constituent in terms of its atmospheric concentrations and biological effects. O_3 is rapidly formed in the atmosphere on warm, sunny days from the reactions of volatile organic compounds (VOC's) with nitrogen oxides (NO_x). Similar sequences of atmospheric chemical reactions also forms numerous other products. O_3 and NO_2 are the two products for which ambient air quality standards have been promulgated (U.S. Environmental Protection Agency, 1978, 1982).

The available laboratory and ambient air measurements for NO and NO_2 have been reviewed extensively elsewhere (National Academy of Sciences, 1977a; Trijonis, 1978; U.S. Environmental Protection Agency, 1982). Therefore, the results of measurements on these NO_x will not be reviewed in the present work. Other substances which are predominantly formed as combustion products or through biological reactions also will not be considered. It is the behavior of the other products formed by atmospheric photochemical reactions in both laboratory studies and ambient air that will be emphasized in this review.

Biomedical and welfare effects have been reported for a number of products of atmospheric reactions besides O_3 and NO_2. Irritation of the eyes and upper respiratory tract as well as lower airway and pulmonary effects have been associated with formaldehyde and other aldehydes (U.S. Dept. of Health, Education and Welfare, 1970b; National Research Council, 1981) and with peroxyacyl nitrates (PANs) (U.S. Dept. of Health, Education, and Welfare, 1970a; U.S. Environmental Protection Agency, 1978). Quantitative dose–response relationships for these products relative to O_3 are not available (National Research Council, 1981; U.S. Environmental Protection Agency, 1978). Welfare effects such as plant damage and visibility degradation have been associated with products of atmospheric reaction at concentrations below those associated with the health

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effects of oxidants or O_3. PANs are the most phytotoxic of the known oxidants (U.S. Environmental Protection Agency, 1978). Sulfate and to a lesser extent nitrate aerosols which are formed in the atmosphere account for most of the increases in light scattering and degradation of visibility (Leaderer *et al.*, 1978; Trijonis and Yuan, 1978a,b; White and Roberts, 1977). Similarly, sulfate aerosols and nitrates have been associated with acid deposition effects (Altshuller *et al.*, 1980).

The term 'oxidants' has been widely used for many years. The term is usually operationally associated with the response characteristics of particular oxidant analyzers or manual methods for oxidants (National Academy of Sciences, 1977b; U.S. Environmental Protection Agency, 1978). However, each measurement technique has a relatively unique pattern of responses. Positive, but not uniform responses occur to O_3, N_2, PANs and to some other peroxides. Reductants such as SO_2 cause negative responses.

Most of the other products of atmospheric reactions do not behave as oxidants in any of the oxidant measurement procedures. Aldehydes, ketones, acids such as formic and nitric acid, as well as aerosol products are examples of products which would not cause positive responses in oxidant measurement procedures. Therefore, the term 'oxidant' is inappropriate in relationship to most of the products of atmospheric reactions.

Photochemically induced atmospheric processes are only one type of atmospheric process capable of forming products. In particular, sulfate aerosols can be formed by other processes, especially those involving reactions within droplets in clouds, rain, fogs and mists. Oxidizing materials as O_3 and H_2O_2 are involved in reactions with SO_2 within droplets (Beilke and Gravenhorst, 1978; Hegg and Hobbs, 1978). The O_3 and H_2O_2 in the droplets can originate as a result of homogeneous photochemical atmospheric processes of concern in this review.

Several of the types of products formed in the atmosphere also can be emitted to the atmosphere from combustion and/or industrial sources. Such chemical species include formaldehyde and sulfates. However, such primary emissions tend to contribute to atmospheric loadings on a localized basis.

Most products of atmospheric photochemical reactions would be expected to occur at higher concentrations in urban areas than over rural areas. Such geographical distributions might be expected because of the combined effects of higher rates within urban areas and the limited lifetimes of most products because of rapid photooxidation in the atmosphere along with removal by dry deposition. However, there is evidence for long-range transport not only of O_3, but also of fine particle species formed by atmospheric reactions (U.S. Environmental Protection Agency, 1981).

A substantial number of individual products and groups of products have been measured in special ambient air studies of limited duration. However, only occasionally have products other than O_3, NO_x and some aerosol species been routinely monitored. Some monitoring of formaldehyde, aldehydes and PAN has been carried out (Cleveland *et al.*, 1977; Dickerson, 1961; Pitts and Grosjean, 1979). Nevertheless, widespread monitoring of products other than O_3 and NO_2 may be impractical. Therefore, it is of interest to evaluate how other products vary in the atmosphere in relation to O_3. In other words, can O_3 be used as an acceptable surrogate for all or a number of these other products. If so, trends in O_3 concentration would serve to indicate trends in other products.

Chemical mechanisms and chemical kinetic models of photochemically induced atmospheric reactions will not be discussed in this review. There are many existing reviews on this subject (Leighton, 1961; Calvert and McQuigg, 1974; Demerjian *et al.*, 1974; Baldwin *et al.*, 1977; Carter *et al.*, 1979; Whitten *et al.*, 1979, 1980). It is possible through such mechanisms to qualitatively account for all of the reaction products measured in laboratory and in atmospheric studies. Quantitative predictions of product concentrations of O_3, NO_2 and other inorganic and organic products can be made. Two recent examples are the studies reported by Atkinson *et al.* (1982) and by Killus and Whitten (1982).

The products formed in laboratory photooxidations of mixtures of various complexity of HCs and aldehydes with NO_x will be discussed by class of precursor compound. Laboratory photooxidations of more complex synthetic mixtures and of automobile exhaust mixtures will be considered, with respect to reactant–product relationships. Product formation from solar irradiation of atmospheric samples also will be discussed. These topics will be followed by a detailed review of available ambient air measurements on individual products of photochemical atmospheric reactions conducted in the United States, Europe, Japan, and in maritime air. Finally, an evaluation of the concentrations of combinations of other such products in the atmosphere relative to O_3 will be made.

2. LABORATORY STUDIES

2.1. *Reaction products from simulated solar irradiations of single HCs or aldehydes with* NO_x

A large number of laboratory studies have been reported on systems involving mixtures of a single HC or aldehyde with NO, NO_2 or both NO_x in the ppm range in air. Light sources simulating the distribution of solar radiation particularly in the near ultraviolet are utilized to provide continous irradiations for periods of hours. Various reactors have been fabricated with differing materials of construction and different surface-to-volume ratios.

O_3 and NO_2 are consistently reported as products provided that the irradiations are continued long enough at appropriate ratios of the reactants. Since O_3

and NO_2 have received much discussion as major products of these reactions, they will not receive further consideration in the discussion below.

The products identified vary with class of organic compound and structural features of individual organic compounds. The products formed will be discussed for the following classes of organic compounds: (1) alkanes, (2) alkenes, (3) alkyl benzenes and (4) aldehydes.

Alkanes. On a carbon ppm basis, alkanes can constitute the largest single fraction of atmospheric HCs (Kopczynski *et al.*, 1972; Lonneman *et al.*, 1974). Alkanes react relatively slowly in the ambient air and in laboratory simulation studies.

The *n*-butane–nitrogen oxide system has been investigated much more completely than other alkane–NO_x systems. Altshuller *et al.* (1969) reported 11–19% conversions to products after a 6-h irradiation period. Percentage conversions of *n*-butane increased with decreasing initial *n*-butane concentrations. The major yields of the major products were as follows: acetaldehyde, 0.6; formaldehyde, 0.3; 2-butanone, 0.25. The minor products identified included PAN, and methyl, ethyl and propyl nitrates.

Subsequently reaction products were measured in studies of the photooxidation of the *n*-butane–nitrogen oxide system by other investigators (Bufalini *et al.*, 1971; Darnell *et al.*, 1976; Pitts *et al.*, 1977a, 1979). The experiments of Bufalini *et al.* (1971) indicated acetaldehyde and methyl ethyl ketone forming early in the irradiation period while formaldehyde and PAN were not produced until later in the irradiations. These investigators also measured CO and CO_2 as products. The following minor or trace products were reported: biacetyl, *tert*-butyl nitrate, ethanol and acetone (Bufalini *et al.*, 1971). In measurements over a wider range of initial concentrations of reactants, CO, 2-butanone and acetaldehyde were observed as major products with intermediate yields of PAN and formaldehyde and small or trace yields of propanal, acetone and alkyl nitrates (Pitts *et al.*, 1977a, 1979). Darnell *et al.* (1976) reported small yields of butyl nitrates.

Studies on the NO_x induced photooxidations of other alkanes are less detailed. In 10–12-h irradiations of 2,3-dimethyl butane with NO_x conversions of 40–60% occurred (Pitts *et al.*, 1979). The major products observed were CO and acetone with minor yields of formaldehyde, acetaldehyde and PAN. Traces of propyl and hexyl nitrates also were reported (Pitts *et al.*, 1979). Altshuller *et al.* (1969) in irradiations of isopentane, 2-methyl-pentane, 3-methyl-pentane, 2,4-dimethylhexane, *n*-nonane and methyl cyclohexane obtained alkane conversions ranging from 10 to 21% after 6-h irradiations. The products identified from the photo-oxidation reactions of these alkanes included acetaldehyde, acetone or butanal, propanal, 2-butanone along with small yields of PANs and methyl nitrate.

When *n*-pentane and *n*-hexane were irradiated with NO_x, alkyl nitrate yields of 0.15 and 0.37 were observed (Darnell *et al.*, 1976). The yields of alkyl nitrates increase with increasing molecular weight of the alkane reacting.

Alkenes. The contribution of alkenes to ambient air loadings on a C ppm basis are substantially less than alkanes (Kopczynski *et al.*, 1972; Lonneman *et al.*, 1974). However, alkenes react much more rapidly than alkanes in atmospheric photooxidation reactions.

Photooxidations of the ethene–NO_x system has been reported in a considerable number of investigations (Altshuller and Cohen, 1964; Gay and Bufalini, 1971; Nicksic *et al.*, 1964; Pitts *et al.*, 1979; Schuck and Doyle, 1959; Schuck *et al.*, 1960; Stephens *et al.*, 1961; Stephens and Scott, 1962). Altshuller and Cohen (1964) obtained average carbon balances of 90 and 66% in two experiments with different NO_x concentrations. Formaldehyde and CO are the major products of ethene photooxidation in all of the investigations conducted. Formaldehyde yields have been reported to vary linearly with ethene concentration (Altshuller and Cohen, 1964). Nitric acid also is formed (Gay and Bufalini, 1971). One or more of the investigators listed above have reported a variety of minor products, but these minor products have not been consistently confirmed.

A considerable number of investigations have been concerned with measurement of product yields in the photooxidation of the propene–nitrogen oxide system (Akimoto *et al.*, 1980; Altshuller *et al.*, 1967; Gay and Bufalini, 1971; Heuss and Glasson, 1968; Pitts *et al.*, 1977a, 1979; Romanovsky *et al.*, 1967; Schuck and Doyle, 1959; Schuck *et al.*, 1960; Spicer and Miller, 1976; Stephens and Scott, 1962; Tuesday, 1963). Major products identified in earlier studies included formaldehyde, acetaldehyde, CO and PAN.

Akimoto *et al.* (1980) in a very detailed compositional study of the propene–NO_x system identified in addition to the products given above, CO_2, formic acid, nitric acid, 1,2-propanediol dinitrate and dinitrogen pentoxide as products. About 95% of the C consumed and 75% of the N from NO_x were associated with products in humidified systems. Stochiometric factors for formaldehyde formed to propene consumed was 1.0 ± 0.1 and for acetaldehyde formed to propene consumed was 0.75 ± 0.1. CO and CO_2 become major products late in the irradiations. PAN was the most important nitrogen containing product exceeding the combined yields of the other nitrogen-containing products (Akimoto *et al.*, 1980).

PAN forms from the reactions of the peroxyacetyl radical produced from acetaldehyde reacting with NO_2. The increasing rate of formation of CO and CO_2 late in the irradiations suggest secondary formation from the aldehydes formed earlier in the reaction period. Very little propene remains available for reaction in the later stages of the irradiation to form CO or CO_2.

Schuck and Doyle (1959) investigated the NO_x induced photooxidations of 20 mono-olefins and diolefins. Infrared spectroscopic measurements of alkene consumption and product formation were reported. While more detailed work has been done more recently on several alkene–NO_x systems, similar recent studies have not been undertaken on most of the alkene–NO_x systems investigated by Schuck and Doyle (1959). Formaldehyde and CO were major products from the photooxidation of most of these systems. PAN although not properly characterized at the time was measured as a major product from most mono-olefin–NO_x systems. Several other aldehydes including acetaldehyde, acrolein, propanal and butanal were identified as major products from the photooxidation of a number of the systems. Ketones were major products from the photooxidation of branch-chain alkenes in the presence of NO_x. Relatively good C balances were reported. The percentage of reacted C atoms accounted for were as follows: butenes, 58–93; pentenes and hexenes, 63–100; conjugated diolefins, 64–100. The C balances were poorer for several cycloolefins, higher molecular weight monoolefins and unconjugated diolefins. Additional product measurements have been provided in a number of other investigations (Altshuller *et al.*, 1966; Arnts and Gay, 1979; Gay and Bufalini, 1971; Heuss and Glasson, 1968; Pitts *et al.*, 1979; Schuck *et al.*, 1960; Stephens, 1961; Stephens and Scott, 1962; Tuesday, 1961, 1963). A number of these investigations provided more detailed measurements on the yields of PANs. Gay and Bufalini (1971) demonstrated the presence of nitric acid in the NO_x photooxidation of several alkenes including 1-butene, *trans*-2-butene, 1,3-butadiene and 2-methyl-2-butene. Additional products formed from the photooxidation of diolefins in the presence of NO_x include formic acid, nitric acid, methacrolein and methyl vinyl ketone (Arnts and Gay, 1979).

The monoterpenes such as α-pinene and β-pinene photo-oxidize in the presence of NO_x to form a number of the smaller molecule products discussed above (Arnts and Gay, 1979). However, a number of higher molecular weight products also are formed including *cis*-pinonic acid, *cis*-pinonaldehyde and norpinonic acid from α-pinene photo-oxidations and 3-hydroxynopinone, nopinone and 3-ketonopinone from β-pinene photooxidations (Arnts and Gay, 1979; Hull, 1980; Schwartz *et al.*, 1974).

Alkylbenzenes. On a C ppm basis, alkylbenzenes contribute a substantially larger fraction of atmospheric hydrocarbon loadings than do alkenes, but less than alkanes (Kopczynski *et al.*, 1972; Lonneman *et al.*, 1974). The slower reacting alkylbenzenes are consumed about as fast as the fastest reacting alkanes. The faster reacting alkylbenzenes are consumed as fast as slower reacting olefins such as ethene and propene.

The photooxidation of the toluene-NO_x system has been the subject of a number of investigations (Altshuller *et al.*, 1966, 1970b; Heuss and Glasson, 1968; Kopczynski, 1964; Pitts *et al.*, 1979; Spicer and Jones, 1977; Spicer and Miller, 1976). Early evidence for ring cleavage was provided by the infrared measurements of Kopczynski (1964). Low yields of formaldehyde, acetaldehyde and PAN have been measured by several investigative groups (Altshuller *et al.*, 1966, 1970b; Huess and Glasson, 1968; Pitts *et al.*, 1979). Low or moderate yields of CO, benzaldehyde and peroxybenzoyl nitrate also have been measured (Heuss and Glasson, 1968; Pitts *et al.*, 1979). Spicer and Jones (1977) reported yields of benzaldehyde, PAN, phthalaldehydes, phenol, cresols, benzoyl alcohol and formaldehyde sufficient to account for 96% of the toluene consumed. Spicer and Miller (1976) accounted for 75–90% of the NO_x consumed in toluene–NO_x mixtures mostly as PAN.

Heuss and Glasson (1968) measured only small or trace yields of formaldehyde and PAN from the NO_x induced photooxidation of seven monoalkylbenzenes containing 8 to 10 C atoms. Nitric acid has been reported as a product from photooxidation of isopropylbenzene (Gay and Bufalini, 1971). Heuss and Glasson (1968) measured moderate to high yields of benzaldehyde and small yields of peroxybenzoyl nitrate from those monoalkylbenzenes containing a benzyl group-toluene, ethyl benzene, *n*-propylbenzene, *n*-butylbenzene and isobutylbenzene.

A number of investigators have studied the NO_x induced photooxidation of dialkyl and trialkylbenzenes (Altshuller *et al.*, 1970b; Altshuller and Cohen, 1963a; Darnell *et al.*, 1979; Gay and Bufalini, 1971; Heuss and Glasson, 1968; Pitts *et al.*, 1979; Stephens and Scott, 1962; Takagi *et al.*, 1980). These alkylbenzenes tend to undergo 50% or greater consumptions in 6-h irradiations (Altshuller *et al.*, 1970b; Heuss and Glasson, 1968).

In earlier work formaldehyde and peroxyacetyl nitrate were reported in small to moderate yields from the photooxidation of the *o*-xylene–nitrogen oxide system (Heuss and Glasson, 1968). Takagi *et al.* (1980) carried out a detailed composition analysis of the nitrogen oxide induced photooxidation products of *o*-xylene. Formaldehyde, acetaldehyde, glyoxal, methylglyoxal and biacetyl were identified as low boiling products. Glyoxal was the major low boiling product. The sum of these products accounted for about 45% of the *o*-xylene consumed. The major high boiling products included tolualdehyde, dimethyl phenols and dimethyl nitrobenzene and these products accounted for about 17% of the *o*-xylene consumed.

Formaldehyde and PAN have been measured in small yields from the photooxidation of the *m*-xylene–NO_x system (Altshuller and Cohen, 1963a; Heuss and Glasson, 1968; Stephens and Scott, 1962). Altshuller and Cohen (1963a) also reported evidence of dicarbonyl products. Altshuller *et al.* (1970b) reported a molar yield of 0.25 to 0.3 of formaldehyde and 0.05 to 0.1 of acetaldehyde formed per mole of *m*-xylene consumed. Trace yields of *m*-tolualdehyde also have been reported (Pitts *et al.*, 1979). Nitric acid has been

identified as a product of the nitrogen induced photo-oxidation of *m*-xylene (Gay and Bufalini, 1971).

Formaldehyde and PAN have been reported in small yields from *p*-xylene and 1,3,5-trimethylbenzene (Heuss and Glasson, 1968). Aldehydes other than formaldehyde were measured along with indications of dicarbonyls in the photo-oxidation of the 1,3,5-trimethyl-benzene–NO_x system (Altshuller and Cohen, 1963a).

Heuss and Glasson (1968) carried out the photo-oxidation of several aromatic olefins in the presence of NO_x. They identified the following products from these aromatic olefins: styrene–formaldehyde and benzaldehyde; α-methyl styrene–formaldehyde, acetophenone and benzaldehyde; β-methylstyrene–formaldehyde, acetaldehyde, benzaldehyde and peroxybenzoyl nitrate; allylbenzene–formaldehyde, phenylacetaldehyde and benzaldehyde. Dimitriades and Wesson (1971) also measured peroxybenzoyl nitrate from the photo-oxidation of α-methyl styrene in the presence of NO_x.

Aldehydes. The NO_x photo-oxidation of a number of aldehydes have been investigated (Altshuller and Cohen, 1963b; Bufalini and Brubaker 1971, Dimitriades and Wesson, 1971; Heuss and Glasson, 1968; Kopczynski *et al.*, 1974; Pitts *et al.*, 1979). Aldehydes fall within the same range of rates of consumption as alkylbenzenes, (Kopczynski *et al.*, 1974).

CO, CO_2 and H_2O_2 have been measured as products of the photooxidation of formaldehyde in presence of NO_x (Bufalini and Brubaker, 1971). CO accounted for up to 90% of the formaldehyde consumed with CO_2 accounting for 12–20% of the formaldehyde consumed in several experiments. While formic acid was observed in several experiments, the results were considered to be inconclusive.

From photo-oxidations of acetaldehyde in the presence of various initial concentrations of NO_x, Kopczynski *et al.* (1974) could account on a C ppb basis for 40–60% of the acetaldehyde consumed as PAN and formaldehyde. Methyl nitrate has been detected as a minor product (Kopczynski *et al.*, 1974; Pitts *et al.*, 1979).

In the photo-oxidation of propanal in the presence of various initial concentrations of NO_x, 62 to 95% of the propanal consumed could be accounted for on a C ppb basis (Kopczynski *et al.*, 1974). The major products were acetaldehyde, CO and peroxypropionyl nitrate. From 22 to 58% of the NO_x consumed could be accounted for as peroxypropionyl nitrate, PAN and ethyl nitrate. The rate of PAN to peroxypropionyl nitrate increased with increasing irradiation time and increasing NO_x concentration. These factors probably favor increased formation of PAN through increased availability of NO_2 and peroxyacetyl radical formed acetaldehyde.

Photo-oxidation of acrolein over a range of acrolein and NO_x concentrations for 6-h periods resulted in consumptions of 39–78% of the acrolein (Altshuller and Cohen, 1963b). Formaldehyde was the major product detected with 0.5 mol of formaldehyde formed per mol of acrolein consumed. Chemical and infrared measurements indicate the presence of a glyoxal. Dimitriades and Wesson (1971) measured a trace of PAN as well as a moderate yield of formaldehyde from this system. Crotonaldehyde when photo-oxidized in the presence of NO_x also formed formaldehyde and a moderate yield of PAN (Dimitriades and Wesson, 1971).

In the photo-oxidation of benzaldehyde in the presence of NO_x, HNO_3 and peroxybenzoyl nitrate have been identified as products (Heuss and Glasson, 1968). Dimitriades and Wesson (1971) measured formaldehyde as a minor product of this system, but were unable to detect peroxybenzoyl nitrate. However, these authors were able to measure peroxybenzoyl nitrate from the photo-oxidation of a benzaldehyde–propene mixture in the presence of NO_x.

Dimitriades and Wesson (1971) measured formaldehyde and PAN as trace or minor products of the photooxidation of *o*-, *m*- or *p*-tolualdehyde in the presence of NO_x.

It can be concluded that CO, formaldehyde, acetaldehyde and several other lower molecular weight aldehydes and ketones along with PANs are major products in many of the systems discussed. Other minor organic products reported result from specific structural features of the organic reactants. Several products including CO, formic acid, HNO_3 and H_2O_2 are only occasionally reported as products. The lack of appropriate measurement techniques is likely to explain the lack of a more consistent observation of these products.

2.2. *Product yields from atmospheric photo-oxidations of multicomponent HC–NO_x systems*

The previous section has been concerned with the products measured in photo-oxidations of a single organic substance with NO_x. A number of experiments have been conducted with two or more HCs or other organics irradiated under static conditions in the presence of nitrogen oxides. A significant question is how well the average yields for individual products can be used to reproduce the yields of these same products in irradiations in multicomponent HC–NO_x systems. A series of studies carried out by Pitts *et al.* (1977a, 1979) are particularly useful for making such comparisons. The comparisons to follow will involve determining how well the use of product yields from experiments with individual HCs can be ued to estimate the product yields observed in the photo-oxidations of 7 component H mixtures with NO_x. These experiments also will be used to examine the effects of the initial conditions of the reactants on product yields.

The 7 HCs used in the mixtures were ethene, propene, *trans*-2-butene, *n*-butane, 2,3-dimethylbutane, toluene and *m*-xylene. The composition of the

seven component HC mixtures was varied as well as the total concentrations of the HCs and the ratio of the HCs to NO_x. The average yields of C containing products from single component HC–NO_x systems were compared with those in the seven component-nitrogen systems at the time of peak or maximum O_3 concentration. If the maximum in O_3 concentrations had not quite been reached at the end of the irradiation period, the yields at the end of the irradiation period were used.

The average product yields (the concentration of the product formed divided by HC consumed on a ppmC basis) for the various C-containing products obtained from experiments available (Pitts *et al.*, 1977a, 1979) for each of single HC–NO_x systems were computed. The yields were computed at the time of maximum O_3 concentration. If a maximum in O_3 concentration was not reached in an experiment, the yields were computed at the end of the irradiation period.

The observed and calculated concentrations in ppmC of six products measured for each of the 11 experiments involving photo-oxidations of the seven component HC–NO_x mixtures are given in Table 1. The concentrations of products are summed for each experiment also. The percentages in parentheses are the sum of concentrations in ppmC of the six products divided by the sum of concentrations in ppmC of the reacted HC multiplied by 100. Therefore, these percentages are an indication of the adequacy of the C balances obtained in these experiments.

The concentration of each calculated product entry in the table was obtained either at the time of maximum O_3 concentration or at the end of the irradiation period by multiplying the concentration of reacted HC by the average yield of the product computed from the single HC–NO_x experiments. This approach assumes product yields to be essentially independent of initial concentrations of the reactants throughout the concentration ranges used. It also assumes that no additional significant interaction effects occur in the seven component HC–NO_x systems which could effect product yields.

For PAN, formaldehyde, acetaldehyde and acetone the observed and calculated concentrations are almost always within a factor of 2 of each other and frequently within ± 10–30%. For 2-butanone the observed and calculated concentrations usually were within a factor of 2, but the agreement generally was somewhat poorer than the other organic products. The differences between the observed and calculated concentrations does not appear to indicate any consistent tendency for the calculated values to overestimate or underestimate the observed concentrations. There are significant uncertainties associated with the observed concentrations (Pitts *et al.*, 1979). The overall accuracy of the PAN measurements is given as ± 20% (Pitts *et al.*, 1979). The reliability of the formaldehyde measurements were estimated to be + 10 to −30%. Considerable difficulties were associated with calibrating for and measuring acetaldehyde. Considering these

Table 1. Comparisons of observed and predicted concentrations as ppmC of a number of products at the irradiation time when ozone is at its maximum concentration*

Expt. No.	Carbon monoxide Obs.	Carbon monoxide Calcd	Peroxyacetyl nitrate Obs.	Peroxyacetyl nitrate Calcd	Formaldehyde Obs.	Formaldehyde Calcd	Acetaldehyde Obs.	Acetaldehyde Calcd	Acetone Obs.	Acetone Calcd.	2-Butanone Obs.	2-Butanone Calcd	ΣObs.	ΣCalcd
231	0.21	1.38	0.18	0.19	0.42	0.44	0.06	0.25	0.54	0.77	0.14	0.20	1.55(29%)	3.23(60%)
232	0.27	0.75	0.08	0.10	0.14	0.12	0.19	0.18	0.48	0.59	0.15	0.17	1.31(44%)	1.91(64%)
233	0.27	0.64	0.07	0.09	0.15	0.14	0.14	0.16	0.30	0.49	0.08	0.13	1.01(40%)	1.65(66%)
237	0.50	0.94	0.17	0.15	0.38	0.32	0.23	0.19	0.58	0.43	0.19	0.12	2.05(58%)	2.15(61%)
238	1.65	1.19	0.22	0.16	0.35	0.47	0.22	0.21	0.77	0.54	0.28	0.16	3.49(77%)	2.73(60%)
241	0.59	0.57	0.09	0.07	0.14	0.19	0.11	0.10	0.27	0.24	0.11	0.07	1.31(66%)	1.24(63%)
242	0.64	1.07	0.25	0.21	0.65	0.50	0.33	0.20	0.21	0.18	0.07	0.04	2.15(51%)	2.20(53%)
243	0.62	0.90	0.20	0.17	0.57	0.57	0.29	0.20	0.10	0.12	0.09	0.05	1.89(50%)	2.01(54%)
245	0.86	1.16	0.30	0.26	0.64	0.67	0.27	0.21	0.21	0.23	0.10	0.05	2.38(44%)	2.58(47%)
246	0.89	0.86	0.14	0.11	0.08	0.15	0.15	0.17	0.65	0.68	0.17	0.18	2.08(62%)	2.15(64%)
247	0.60	0.72	0.19	0.14	0.33	0.36	0.13	0.11	0.20	0.14	0.04	0.04	1.49(50%)	1.51(51%)
												Range (%)	29–77	47–66
												Average	52	58

*Computed from Pitts *et al.* (1979).

uncertainties, the agreement between observed and calculated concentrations of the organic products usually are reasonable. The assumptions made in obtaining the calculated concentrations appear to be acceptable.

For CO the agreement between observed and calculated concentrations was highly variable. In most experiments the agreement was good to fair. In several experiments, 231, 232 and 233, the calculated concentrations were much higher than the observed concentrations (Table 1). The CO measurements were estimated to be reliable to about ± 10%. In almost all of the experiments, there was a substantial concentration of CO present before the experiment began. In the experiments with the poorest agreement, the increase in CO concentration during irradiation was only 10 to 20% of the initial CO concentration. This circumstance increases the uncertainty in the observed CO concentrations.

Summing over the six major products the agreement between observed and calculated yields is good for seven of the experiments (237, 241, 242, 243, 245, 246, 247). The overall average sum of yields from the experimental results accounting for 52% of HC consumed compares reasonably well with the 58% value from calculated yields (Table 1). The larger differences in overall product yields in experiments 231, 232, 233 and 238 are due to a large extent to the discrepancies in the observed and calculated CO results as discussed above. In general, it appears that the average yields obtained from individual system irradiation results give reasonable prediction (within ± 20–30% for about 2/3 of the 66 sets of comparisons).

The effects of variations in initial reactant conditions on product yields, which can be considered based on the experiments of Pitts *et al.* (1979), are as follows: (1) initial HC concentrations varied with initial NO_x concentration and HC composition fixed, (2) initial NO_x concentration varied with initial HC concentration and composition fixed, (3) initial HC and NO_x concentrations varied concurrently with the HC composition fixed and (4) initial HC compositions varied with the HC and NO_x concentration fixed.

Since detailed experimental measurements for reactants and products with irradiation time are available (Pitts *et al.*, 1979), the following measures of product yields were considered: (a) concentrations of other products at the time of maximum O_3 concentration and (b) dosages of products, in ppm *X* minutes, during irradiation periods. The dosages are obtained by plotting the product concentration values with irradiation time up to 360 min and integrating under the curve. These product yields were computed for O_3, PAN and formaldehyde. The results are given in Table 2 for the appropriate pairs of experiments. The following conclusions can be derived.

(1) Reductions in initial HC concentrations in experimental pair I result in substantial decreases in the concentrations of products and even larger decreases in the dosages of products.

Table 2. Maximum product concentrations and product dosages from seven HC/NO_x experiments as a function of varying initial hydrocarbon concentration and composition and/or NO_x concentration

Expt. pairs (Numbers)	Variation of interest	Initial concn of reactants HC, ppmC	NO_x, ppm V	Hydrocarbon composition %*	Max. concn of products, ppm V O_3	PAN	CH_2O	Dosages, ppm min^{-1} O_3	PAN	CH_2O
I(237,241)	Reduce HC concentration	10.5	0.48	Alkane, 65	0.65	0.086	0.38	159	21	48
		5.0	0.49	Olefin, 23	0.41	0.047	0.14	54	6.5	17
				Aromatic, 12						
II(232,233)	Reduce NO_x concentration	9.3	0.49	Alkane, 87	0.31	0.040	0.14	41	5.5	30
		9.5	0.10	Olefin, 8	0.33	0.034	0.14	92	8.4	36
				Aromatic, 5						
III(237,238)	Reduce NO_x concentration	10.1	0.95	Alkane, 65	0.69	0.11	0.34	76	11.5	38
		10.5	0.48	Olefin, 23	0.60	0.84	0.40	159	21	47
				Aromatic, 12						
IV(245,247)	Reduce HC and NO_x concentration	12.9	0.99	Alkane, 25	0.89	0.15	0.64	213	44	195
		6.1	0.51	Olefin, 39	0.66	0.095	0.30	161	27	75
				Aromatic, 36						
V(232,237)	vary hydrocarbon composition	9.3	0.49	high alkane, as above	0.31	0.040	0.14	41	5.5	30
		10.5	0.48	intermediate, as above	0.65	0.085	0.38	159	21	48

(2) Reductions in initial NO_x concentrations in experimental pairs II and III result in small or negligible changes in the concentrations of products. Dosages of these products increase substantially with decreases in NO_x concentrations.

(3) Concurrent reductions in initial HC and NO_x concentrations in experimental pair IV result in decreases in both the concentrations and dosages of products.

(4) Reductions in HC, NO_x, or both reactants usually resulted in different percentage changes in the concentrations and the dosages of each product compared to the other products.

(5) Replacement of alkanes by more reactive olefins and aromatics in experimental pair V results in substantial increases in the concentrations of products and even larger increases in the dosages of O_3 and PANs.

The increases in dosages with decreasing NO_x concentration are associated with suppression of product formation in the earlier portions of the irradiation periods by the higher initial concentrations of NO. The decreases in concentrations and dosages of products resulting from concurrent reductions of initial HC and NO_x concentrations are not as large as obtained from only the reduction of HC concentration. The same initial suppressive effect of NO is considered likely to account for this result also. Although directional effects usually were the same for the three products, the quantitative changes in concentrations and dosages of peroxyacetyl nitrate and formaldehyde often differ appreciably compared to those for O_3. The results for these products should not be extrapolated to other products. It also is important to note that the HC to NO_x concentration ratios range from 10 to 95. This is an appreciably higher range of ratios than was used in the irradiated and exhaust studies to be discussed in the next section.

2.3. *Product yields from simulated solar irradiations of auto exhaust mixtures in smog chambers*

Several studies have involved measurement of the products of simulated atmospheric solar irradiations of diluted auto exhaust over a range of initial conditions of HC and NO_x concentrations in smog chambers. The results of these studies allow, (a) consideration of the yields of several major products, (b) comparison of yields of other products with O_3 and (c) evaluation of reactant–product relationships.

Leach *et al.* (1964) reported measurements for formaldehyde, acrolein and total aldehydes during simulated solar irradiations under dynamic conditions of an auto exhaust mixture. Measurements were obtained at three different initial concentration levels, 3, 6 and 12 ppmC, and at five different HC to NO_x ratios. The formaldehyde and acrolein concentrations constituted 50 and 5%, respectively of the concentrations of the total aliphatic aldehydes. When the results were averaged at each concentration level, a linear relationship was obtained between both the formaldehyde and total aliphatic aldehyde concentrations. The linear relationship is consistent with the use of averaged yields in the previous discussion of multicomponent systems.

Comparisons of formaldehyde concentrations with oxidant concentrations (Leach *et al.*, 1964; Korth *et al.*, (1964) are given in Table 3. The oxidant yields were found to be more sensitive to changes in reactant ratios than were the aldehyde yields. Oxidants were not formed in the lower reactant ratio experiments. As the initial NO_x concentration was decreased at constant initial HC concentration, oxidant concentrations increased substantially, but formaldehyde concentrations remained substantially unchanged. The for-

Table 3. Comparisons under various initial conditions of oxidant and formaldehyde concentrations produced in study of irradiated auto exhaust*

Average irradiation time	Initial concentrations HC, ppmC	NO_x, ppm	Product concentrations, pphm Oxidant	Formaldehyde	(Formaldehyde/Oxidant) × 100
120 min	3	1/4	31	10	32
	3	1/2	23	10	43
	6	1/2	36	17	47
	12	1/2	52	32	62
	3	1	0	8	—
	6	1	19	20	105
	12	1	43	32	74
	3	2	0	6	—
	6	2	0	17	—
	12	2	7	29	24
180 min	3	1/2	25	10	40
	6	1/2	41	20	49
	3	1	0	9	—
	6	1	10	17	170
	12	1	53	36	68
	6	2	0	15	—
	12	2	4	40	1000

* Korth *et al.* (1964).

maldehyde concentration yields constituted a substantial percentage of oxidant concentration yields under all conditions and exceeded oxidant yields when oxidant was suppressed.

The substantial increases in oxidant concentration with reductions in NO_x concentration, Table 3, contrast with the smaller variations obtained in the synthetic mixtures under static irradiation conditions shown in Table 2. However, this difference may result from the higher HC to NO_x ratio range for the experiments considered in Table 1.

Dimitriades (1970) has obtained measurements of products from the simulated solar irradiations of diluted automobile exhaust over a large concentration range for HC, 0.2–5 ppmC and NO_x, 0.08–1.38 ppm, and reactant, ratios 1:1 to 12:1. The chamber was operated in a static mode. Measurements were reported for oxidant, PAN, formaldehyde and NO_2 in terms of dosages defined as the products of concentration times irradiation time, (ppm min).

The effects of changes in initial reactant concentration on the product dosages of oxidant, PAN and formaldehyde can be evaluated from this report (Dimitriades, 1970). Computations were made from the results tabulated of changes in the product dosages relative to variations in initial reactant concentrations. The changes were computed on a percentage basis relative to a baseline mixture selected from each related set of four irradiation experiments. The baseline mixture was the mixture in each set containing the highest concentration of HC, and/or NO_x concentrations. Based on these computations the following conclusions results were obtained.

(1) When the initial HC concentrations are reduced, with the initial NO_x concentrations fixed. (a) The product dosages of oxidant, PAN and formaldehyde also decrease. (b) On a quantitative basis relative to the percentage reductions in initial HC concentration, (1) the percentage decreases in PAN dosages are larger than those in oxidant dosages. The exact relationships of the oxidant and PAN dosages to HC concentrations are very dependent on the initial NO_x concentration, (2) the percentage decreases in formaldehyde dosages either can be greater or less than those in oxidant dosages. The formaldehyde dosages are proportional to initial HC concentrations (Fig. 1). A moderate sensitivity to NO_x concentration is evident, but sensitivity is less than that shown by the oxidant dosages. (The non-zero intercept on the formaldehyde dosage axis in Fig. 1 was attributed to chamber contamination.)

Oxidant, PAN and formaldehyde dosages show the same directional characteristics. The quantitative relationships of products to reactants are different for each product.

(2) When the initial NO_x concentrations are reduced, with the initial HC concentrations fixed. (a) The product dosages of oxidant, PAN and formaldehyde increase. (b) On a quantitative basis relative to the percentage reductions in initial NO_x concentration, (1) the percentage increases in the dosages of PAN usually are larger than those in oxidant dosages and (2) the percentage increases in dosages of formaldehyde are smaller than those in oxidant dosages.

Oxidant, PAN and formaldehyde do not show the same directional characteristics as NO_x. The quantitat-

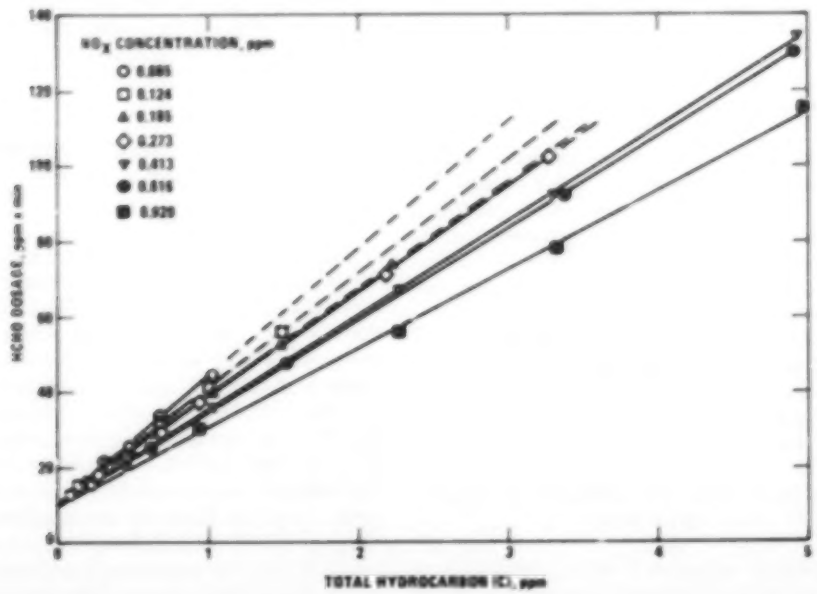

Fig. 1. Formaldehyde dosages as a function of initial total hydrocarbon concentrations at various initial NO_x concentration levels.

ive relationships of products to reactants are different for each product.

(3) When the initial HC and the initial NO_x concentrations are reduced at fixed ratios of these reactants. (a) The directional characteristics are different for each product. (1) The oxidant dosages decreased when the reactant ratios were greater than 3.6:1, but increased when the ratios were less than 3.6:1, (2) the PAN dosages decreased when the reactant ratios were greater than 2.4:1, but increased when the ratios were less than 2.4:1 and (3) the formaldehyde dosages decreased throughout the range of reactant ratios utilized in the study.

(b) On a quantitative basis relative to the percentage reductions in initial HC and initial NO_x concentration. (1) the percentage decreases in the dosages of PAN were greater than those in oxidant dosages and (2) the percentage decreases in formaldehyde dosages were greater than those in either oxidant or PAN dosages.

Oxidant, PAN and formaldehyde show different and varied directional characteristics relative to the reactants. The quantitative relationships of products to reactants are different for each product.

The results of this study (Dimitriades, 1970) indicate that the product yields expressed as dosages may or may not show the same directional characteristics as the reactants. Even when the dosages of products do show the same directional characteristics as the reactants, the quantitative relationships were different for each product. The directional characteristics for products, expressed as dosages, obtained from the experiments of Pitts *et al.* (1979) are consistent with those obtained from the measurements of Dimitriades (1970).

Dimitriades *et al.* (1973) irradiated diluted auto exhaust obtained from a vehicle operated with gasolines representing a wide range of HC compositions. At the 6:1 ratio of HC to NO_x used, the range of product concentrations obtained as gasoline composition was varied are as follows: O_3, 0.56–0.96 ppm; PAN, 0.045–0.12 ppm; peroxypropionyl nitrate, 0.003–0.024 ppm; formaldehyde, 0.50–0.84 ppm. The peroxyacetyl nitrate concentrations were 7–14% of the O_3 concentrations, while the formaldehyde concentrations were from 67 to 125% of the O_3 concentrations depending on fuel composition. The peroxypropionyl nitrate concentrations were from 7 to 25% of the PAN concentrations depending on fuel. The lowest yields were measured when gasolines containing very low olefin contents were used. These results show a significant effect of initial HC composition on product yield.

3. PRODUCTS ANALYSES FROM IRRADIATED AMBIENT AIR SAMPLES

A technique intermediate between investigations of laboratory systems and analysis of ambient air samples with time of day has been utilized (Altshuller *et al.*, 1970a; Kopczynski *et al.*, 1972). This technique involves collecting morning samples of ambient air in a plastic bag transparent to solar radiation and conducting analysis of reactants and products with time during the day. Altshuller *et al.* (1970a) reported both reactant and product analyses on ambient air samples collected in Tedler film bags on 6 days during October–November 1967 in downtown Los Angeles. Samples were collected between 0700 and 0800 h and irradiated with sunlight over a 6th period. Maximum oxidant, PAN and formaldehyde concentrations after irradiation were obtained. The range of maximum daily concentrations of the products was as follows: oxidant, 180–300 ppb; PAN, 26–62 ppb; net formaldehyde 130–490 ppb. PAN concentrations were from 10 to 21% of the oxidant concentrations. The formaldehyde concentrations were from 62 to 200% of the oxidant concentrations. These results are consistent with those in the smog chamber studies with irradiated automobile exhaust (Dimitriades, 1970; Dimitriades *et al.*, 1973; Korth *et al.*, 1964).

A subsequent study (Kopczynski *et al.*, 1972) was carried out on 14 days during September–November 1969 in downtown Los Angeles. Similar procedures were used, formaldehyde was not measured. The ranges of maximum daily concentrations were as follows: oxidant, 10–390 ppb; PAN, 8–97 ppb. The correlation coefficient between maximum oxidant and maximum PAN concentrations was 0.71. However, this relationship was poor at the high end of the oxidant concentration range. For the irradiations producing the three highest maximum oxidant concentrations, 380, 390, 390 ppb, the maximum PAN concentration ranged from 25 to 97 ppb. If 6 irradiation days with very low oxidant concentrations were excluded, the PAN concentrations on the average were 13 per cent of the oxidant concentrations. The percentage is within the range obtained from the previous study (Altshuller *et al.*, 1970a).

4. AMBIENT AIR STUDIES OF ATMOSPHERIC PHOTOCHEMICAL PRODUCTS

4.1. *Aldehydes and ketones*

Atmospheric chemistry. Aldehydes and ketones are formed from most types of HCs either by reactions with hydroxyl radicals or O_3, (National Research Council, 1981). Higher molecular weight aldehydes photooxidize to form lower molecular aldehydes as products, (Kopczynski *et al.*, 1974; National Research Council, 1981). Aldehydes also are consumed by direct photolysis in sunlight (Leighton, 1961; National Research Council, 1981). Although formation of aldehydes through reactions of alkenes with ozone tends to occur later in the day as O_3 concentrations increase, reactions of HC with hydroxyl radicals can occur throughout the daylight hours. In addition, aldehydes and ketones are emitted to the atmosphere as combustion products, (National Research Council, 1981). Consequently, significant concentration levels of alde-

hydes and ketones should be presented throughout the day. The diurnal concentration curves for aldehydes and ketones should be flatter than are the diurnal concentration curves for O_3. Very little appears to be known about the deposition of aldehydes and ketones (Schmel, 1980). No rapid modes of dry deposition are known; therefore, these compounds could persist through the night.

Methods of measurement of aldehydes. A substantial number of different methods of measurement of aldehydes have been used to analyze aldehydes. The bisulfite method was used in studies in the 1950s and early 1960s, while the high performance liquid chromatography and long path Fourier transform infrared spectroscopy have been used in recent years. The chromotropic acid method for formaldehyde is the procedure most consistently used through the last 20 years.

The bisulfite method (sulfoxylate method) has been widely used to analyze carbonyl compounds in air pollution and industrial hygiene (Goldman and Yagoda, 1943). The sensitivity of this method is not high, so large samples have to be collected for analysis of atmospheric samples. The sampling procedure routine in use can result in substantial losses of C_4 and higher aldehydes and of ketones (Wilson, 1958).

A spectrophotometric method for aldehydes based on use of the 3 methyl-2-benzothiazolone hydrazone reagent, MBTH, was developed in the early 1960s, (Sawicki *et al.*, 1961). The method is sensitive and applicable to ambient air analysis (Altshuller and McPherson, 1963; Altshuller and Leng, 1963; Hauser and Cummins, 1964). The blue dye formed with formaldehyde has molar absorptivities at 635 and 670 nm which are 25% higher than the dyes formed with acetaldehyde and other straight-chain aliphatic aldehydes and as much as 300% higher than the dyes formed with branch-chain aldehydes, unsaturated aldehydes and dialdehydes. Therefore, this method tends to underestimate the concentrations of total aldehydes if calibrated in terms of formaldehyde. Since calibration with other individual aldehydes is not a satisfactory procedure either, the multiplication of concentrations obtained from ambient air analyses by a factor of 1.25 has been suggested (Altshuller and Leng, 1963). This factor was based on a reasonable typical composition as assumed for ambient air aldehydes. The aldehyde values obtained from the MBTH method have been multiplied by this factor to give the values tabulated in Table 5.

Individual aldehyde and ketones have been analyzed by high performance liquid chromatography (HPLC) (Fung and Grosjean, 1981; Grosjean *et al.*, 1980; Kuntz *et al.*, 1980). The carbonyls are collected on inpingers containing 2,4-dinitrophenylhydrazine which reacts to form the hydrazones. It should be possible by HPLC to separate and analyze for a large number of individual aldehydes and ketones and sum their individual concentrations to obtain total carbonyl concentrations. In practice, most of the studies in recent years reporting ambient air measurements by HPLC have only reported measurements for formaldehyde and for acetaldehyde.

The method of measurement most frequently used to analyze for formaldehyde in the ambient atmosphere is the chromotropic acid (CA) method (Altshuller *et al.*, 1961). There are a number of potential interferences with the CA method. However, they do not appear to constitute a significant problem under ambient air conditions based on the intercomparisons of methods to be discussed later.

Formaldehyde can be measured in the ambient atmosphere by use of long path Fourier transform infrared spectroscopy, LP-FTIR (Hanst, 1971; Hanst *et al.*, 1975). The infrared absorption of formaldehyde at 2779 and 2781.5 cm^{-1} is used. A detection limit of 6 ppb has been obtained with a 1 km path length (Tuazon *et al.*, 1981b).

A spectrophotometric method for acrolein based on use of 4-hexylresorcinol reagent was developed in the early 1960s by Cohen and Altshuller (1961). Acrolein reacts with 4-hexylresorcinol to form a blue chromogen of high color intensity and adequate stability.

Intercomparison of methods. An intercomparison study of methods for measurement of formaldehyde were conducted in several phases during June 1980 at California State University in Los Angeles and in September–October, 1980 at Harvey Mudd College in Claremont, CA (Grosjean and Kok, 1981). The methods intercompared were the chromotropic acid method, high performance liquid chromotography and a chemiluminescent method. The chromotropic acid procedure involved collection in aqueous bisulfite solution. The chemiluminescent method used is based on the reaction of formaldehyde with 3, 4, 5-trihydroxybenzoic acid resulting in emissions at 643, 702 and 762 nm (Kok, 1982).

In the laboratory tests with synthetic formaldehyde, acetaldehyde and with binary mixtures in air, reasonably good agreement was obtained among methods. Better agreement was obtained by use of a vacuum rack dynamic dilution system rather than use of a static mode with Teflon bags. However, the minimum aldehyde concentrations used with the dynamic dilution system were above 100 ppb. The regressions obtained from the measurements with the chemiluminescent method resulted in a larger slope than obtained for the other methods as well as a negative intercept.

In the intercomparisons made using ambient air samples collected at California State University during 17–20 June 1980 and at Harvey Mudd College during 19 September–8 October 1980 more scatter in results was observed than in the laboratory intercomparisons. The formaldehyde concentrations measured by the chemiluminescent method were consistently lower by a factor of 3 than from the other methods suggesting negative interference problems (Grosjean and Kok, 1981; Kok, 1982).

Formaldehyde was measured concurrently by the chromotropic acid method and by HPLC at a site in Pittsburgh, PA during 15–16 April 1981 and Chicago, IL during 27–28 April 1981 (Singh *et al.*, 1982). The average formaldehyde concentrations agreed to within 5% with each other. The individual values measured were within ± 30% of each other.

In Columbus, OH, at the Fort Hayes site, 16 concurrent samples were obtained by both the chromotropic acid method and high performance liquid chromotography (Joshi *et al.*, 1981). The average formaldehyde concentration for this subset of samples was 7.3 ppb from the chromotropic acid method and 7.9 ppb from HPLC. Thirteen of the 16 values were within ± 50% of each other.

Measurements of total aldehydes and of carbonyl compounds in the South Coast Air Basin. The bisulfite method was used to measure 'aldehydes' at a number of monitoring sites of the County of Los Angeles, CA in the 1950s (Dickerson, 1961). The average aldehyde concentrations measured in 1955–1957 during daylight (0630–1830) are given in Table 4. The percentage that aldehyde concentrations constitute of oxidant concentrations averaged over the same time periods also are tabulated. The average aldehyde concentrations did not vary greatly among stations in a given year: 1955, 110–150 ppb; 1956, 90–130 ppb; 1957, 40–60 ppb. The aldehyde concentrations were substantially lower in 1957 than 1955. The maximum aldehyde concentrations reported at these sites (not tabulated) varied from 220 to 1870 ppb. These maximum concentrations were not distributed as were the average concentrations. Several of the maximum values reported in 1957 were among the highest measured in the 1955–1957 period. The diurnal curves (Dickerson, 1961) were relatively flat with a 'weak' concentration maximum late in the morning and sometimes in the late afternoon or early evening. Although concentrations of aldehydes decreased at night, the decrease was by a factor of 2 or less. These small diurnal variations result in the 23-h average concentration values being only 10–20% less than the average daylight concentrations at the same sites.

The average and maximum concentrations of total aldehydes and of formaldehyde obtained from a number of subsequent field studies are tabulated in Table 5. These studies included oxidant or O_3 measurements. The aldehyde of formaldehyde concentrations were used along with the oxidant or O_3 concentrations to compute (aldehyde/O_x or O_3) × 100 or (formaldehyde/O_x or O_3) × 100 values. The percentages computed from concentrations averaged over an entire study and also at the times of maximum oxidant or O_3 concentrations are tabulated in Table 5. These results will be discussed later in this section. When

Table 4. Summary of average aldehyde concentrations for August to November periods at monitoring sites in County of Los Angeles, CA*

Site	No.	Year	Concentrations, ppb V†	(Ald/Oxidant) × 100†
Downtown Los Angeles	1	1955	110	110
	1	1956	90	90
	58	1956	80	133
	58	1957	40	57
West Los Angeles	2	1955	130	260
	2	1957	30	100
	61	1957	40	57
Pasadena	56	1955	120	92
	4	1956	100	143
	4	1957	50	83
Rivera	5	1957	40	67
Azuza	7	1955	140	200
	60	1957	40	50
Burbank	9	1955	150	300
	9	1957	60	75
Reseda	11	1956	130	325
Lennox	12	1957	60	120
Torrance	13	1956	110	220
Vernon	15	1955	110	138
	15	1956	90	129
	15	1957	60	120
Edison El. Seg.	59	1957	50	83

* Concentrations from Tables XIV and XV in Dickerson (1961).
† Daylight hours (0600–1830).

Table 5. Ambient air measurements of formaldehyde and aldehydes at urban sites in the United States

Site/Ref.	Period of year (No. of days)	Hours of day	Comp(s)	Concentrations (ppb) Av.	Max	(Ald or CH_2O)/(O_x or O_3) × 100 Av.	O_x or O_3 max
Downtown Los Angeles, CA Renzetti and Bryan (1961)	July–Nov. 1960 (15)	0900–1200	formaldehyde*	45	130	30	20
			aldehydes†	150	360	90	60
S. Pasadena, CA Renzetti and Bryan (1961)	July–Nov. 1960 (16)	1300–1600	formaldehyde*	30	70	15	15
			aldehydes†	110	270	50	45
Downtown Los Angeles, CA Altshuller and McPherson (1963)	Sept.–Nov. 1961 (31, 2)	0700–1600	formaldehyde*	40	160	45	30
			aldehyde‡	65	175	90	90
Huntington Park, Scott Research Lab (1969)	Oct. 1968 (2)	0740–1445	formaldehyde*	70	135	105	NA§
			aldehyde‡	100	175	160	NA§
EL Monte, CA Scott Research Lab (1969)	Oct. 1968 (2)	0545–1330	formaldehyde*	50	90	45	NA§
			aldehydes‡	90	150	75	NA§
Los Angeles, CA (Cal. State Univ.) Grosjean and Kok (1981); Grosjean (1982)	June 1980 (4)	morning to evening	formaldehyde*,‖	21, 20	35, 39	25	15
Los Angeles, CA (Cal. State Univ.) Hanst *et al.* (1982); Grosjean and Kok (1981)	June 1980 (7)	morning to evening	formaldehyde¶	44	71	60	25
Claremont, CA (Harvey Mudd College) Tuazon *et al.* (1981a,b)	Oct. 1978 (5)	late morning to late evening	formaldehyde¶	28	71	30	13
Claremont, CA (Harvey Mudd College) Tuazon *et al.* (1981a)	Aug.–Sept. 1979 (8)	morning to late evening	formaldehyde¶	10	22	15	9
Claremont, CA (Harvey Mudd College) Grosjean and Kok (1981); Grosjean (1982)	Sept.–Oct. 1980 (7)	morning to evening	formaldehyde‖	24	48	15	10
			aldehydes‖	47	49	25	20
Riverside, CA (Univ. Cal., Riverside) Tuazon et al. (1978)	Oct. 1976 (3)	late morning to early evening	formaldehyde¶	8	14	5	3
Riverside, CA (Univ. Cal., Riverside) Tuazon *et al.* (1980)	June, Aug., Oct. 1977 (10)	late morning to evening	formaldehyde¶	19	38	10	9
Houston, TX (Crawford) Joshi (1979); Nitz and Martinez (1982)	Sept.–Oct. 1978 (6)	morning to early evening	formaldehyde*	15	25	80	ID**
			aldehydes‡	28	43	170	ID**
Houston, TX (Clinton Dr.) (Joshi (1979); Nitz and Martinez (1982)	Sept.–Oct. 1978 (7)	morning to after noon	formaldehyde*	8	28	ID‡	ID**
			aldehydes‡	18	50	ID‡	ID**
Houston, TX (Parkhurst) Joshi (1979);	Sept.–Oct. 1978 (7)	morning to early evening	formaldehyde*	7	15	20	ID**
			aldehydes‡	12	20	30	ID

Table 5. (Contd)

Site/Ref.	Period of year (No. of days)	Hours of day	Comp(s)	Concentrations (ppb) Av.	Max	(Ald or CH_2O)/(O_x or O_3) × 100 Av. O_x or O_3	max
Nitz and Martinez (1982)							
Houston, TX (Fuqua)	Sept.–Oct. 1978 (7)	morning to early evening	formaldehyde*	11	27	ID§	ID**
(Joshi (1979); Nitz and Martinez (1982)			aldehydes‡	23	45	ID§	ID
Columbus, OH (Fort Hayes)	Sept.–Oct. 1980 (20)	early morning to after noon	formaldehyde‖	8	23	25	ID**
Joshi *et al.* (1981)			aldehydes‡	17	40	40	ID**
Columbus, OH (WCVO)	Sept.–Oct. 1980 (5)	early morning	formaldehyde‖	10	12	ID§	ID**
Joshi *et al.* (1981)			aldehydes‡	21	16	ID§	ID**
Atlanta, GA (GA Tech)	July–Aug. 1981 (7)	0600–1230	formaldehyde*	8	22	35	ID**
Corse (1981)			aldehydes‡	16	29	70	ID**

* Chromotropic acid method.
† Iodine titration of bisulfite ion.
‡ 3-Methyl-2-benzothiazole hydrazone method.
§ Not available.
‖ High performance liquid chromatography.
¶ Long path Fourier transform infrared spectroscopy.
** Insufficient data.

measurements in a study were available for only aldehyde or formaldehyde concentrations and oxidant or O_3 concentrations were not available, the results are not tabulated in Table 5, but are discussed in the text.

The bisulfite method was used to measure aldehydes in Los Angeles in 1960 (Renzetti and Bryan, 1961). The average and maximum 'aldehyde' concentrations are given in Table 5. The average concentration values obtained in 1960 are within the range of values obtained in 1957 (Dickerson, 1961). The maximum concentrations in the later study may not be comparable to those reported in 1955–1957 because of the shorter period of measurement in the later study.

The MBTH method with the shorter collection period of 1 to 2 h was used to measure aldehydes in downtown Los Angeles, CA in 1961 (Altshuller and McPherson, 1963) and at sites in Huntington Park, CA and El Monte, CA in 1968 (Scott Research Laboratories, 1969). The average and maximum concentrations are given in Table 5.

In a study at Harvey Mudd College in Claremont, CA, HPLC measurements were obtained for several carbonyl compounds on 7 days in the period between 19 September and 8 October 1980 (Grosjean, 1982; Grosjean and Kok, 1981). The average and maximum concentration of the sum of aldehydes measured is given in Table 5.

Measurements of formaldehyde and other individual aldehydes in the South Coast Air Basin. The CA method was used in the study carried out by Renzetti and Bryan (1961) in Los Angeles during 1960. Aliquots for analysis of formaldehyde were obtained from the aqueous bisulfate solutions used for analysis of aldehydes. The average and maximum formaldehyde concentrations obtained at the sampling sites in downtown Los Angeles and South Pasadena are given in Table 5.

Altshuller and McPherson (1963) used the CA method with collection of the ambient air samples in a chromotropic acid solution in sulfuric acid. This mode of sampling increased the sensitivity substantially over collection in aqueous solution. The average and maximum concentrations of formaldehyde at the site in downtown Los Angeles are given in Table 5. The formaldehyde concentrations measured were close to those measured the year before in downtown Los Angeles by Renzetti and Bryan (1961). The diurnal pattern of formaldehyde concentrations showed an increase to maximum concentrations in later morning or early afternoon followed by a moderate decrease by late in the afternoon. The diurnal profile observed was consistent with that obtained by the bisulfite method for 'aldehydes' (Dickerson, 1961).

Measurements were made by the same CA procedure for formaldehyde used by Altshuller and McPherson (1963) in 1968 (Scott Research Laboratories, 1969). The average and maximum formaldehyde concentrations measured at two sites in the Los Angeles Basin (Huntington Park, CA and El Monte, CA) are given in Table 5.

In June 1980, formaldehyde was measured on the

campus of California State College in Los Angeles (Grosjean, 1982; Grosjean and Kok, 1981). Analyses were made both by high performance liquid chromatography and the chromotropic acid method. The average and maximum concentrations obtained by the two methods were in good agreement (Table 5). Formaldehyde also was measured by long path Fourier transform infrared spectroscopy at this same site, but not over exactly the same time periods in June, 1980 (Grosjean and Kok, 1981; Hanst *et al.*, 1982). The formaldehyde concentrations obtained by LP-FTIR were appreciably higher than the concentrations obtained by use of HPLC and the CA method (Table 5).

Formaldehyde was measured using LP-FTIR in Claremont, CA on the campus of Harvey Mudd College in 1978 and 1979 (Tuazon *et al.*, 1981a,b). The average and maximum concentrations of formaldehyde are given in Table 5. Diurnal profiles of formaldehyde were obtained at Claremont (Tuazon *et al.*, 1981b), as in Los Angeles, CA, (Hanst *et al.*, 1982). The results (Figs 2 and 3) are consistent with earlier studies showing a more uniform profile for formaldehyde than O_3.

Formaldehyde measurements were made at Harvey

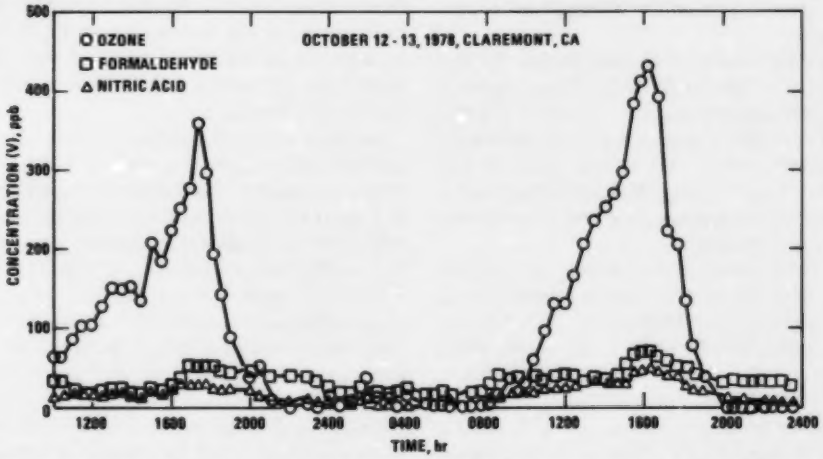

Fig. 2. Diurnal profiles of ozone, formaldehyde and nitric acid during 12–13 October 1978 within Claremont, CA.

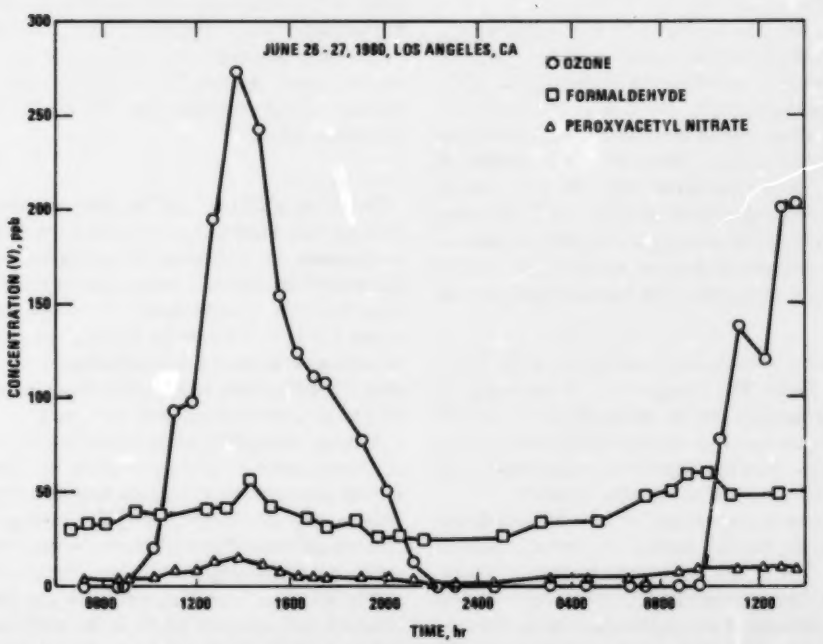

Fig. 3. Diurnal profiles of ozone, formaldehyde and peroxyacetyl nitrate during 26–27 June 1980 within Los Angeles, CA.

Mudd College in Claremont, CA in 1980 by HPLC and the CA method (Grosjean and Kok, 1981). Since more measurements were made by HPLC, the average and maximum concentrations of formaldehyde obtained by HPLC are given in Table 5.

Formaldehyde was measured by LP-FTIR in Riverside, CA on the campus of the University of California, Riverside in 1976 and 1977 (Tuazon *et al.*, 1978, 1980). The average and maximum concentrations are given in Table 5.

Measurements were made by the CA method for formaldehyde in Riverside, CA in July, 1980 (Singh *et al.*, 1982). The average and maximum concentrations of formaldehyde obtained were 19 and 41 ppb, respectively.

The higher formaldehyde concentrations obtained by LP-FTIR at California State University compared to the concentrations obtained at Claremont, CA and Riverside, CA (Table 5), suggest a gradient downward in formaldehyde concentrations from west to east across the Los Angeles Basin. However, such a conclusion may be in doubt because of the lack of concurrent measurements at these sites.

Acrolein was measured in ambient air samples collected at four sites in Los Angeles County during the 1960s (Altshuller and McPherson, 1963; Renzetti and Bryan, 1961; Scott Research Laboratories, 1969). The average and maximum acrolein concentrations, in ppb, for acrolein by site and year obtained were as follows: Downtown Los Angeles, CA (1961) 5, 11; (1963) 7, 14; S. Pasadena, CA (1961) 6, 11; Huntington Pk, CA (1968) 6, 11; El Monte, CA (1968) 4, 8. These concentrations are in good agreement among sites over this time period, 1961–1968.

Acetaldehyde was measured by high performance liquid chromatography at California State University in Los Angeles, CA during 1980, (Grosjean, 1982; Grosjean and Kok, 1981). The average and maximum concentrations measured were 8 and 24 ppb. At a site at Harvey Mudd College, Claremont, CA a number of aldehydes were measured by HPLC during September–October 1980 (Grosjean, 1982; Grosjean and Kok, 1981). The average and maximum concentrations in ppb are as follows: acetaldehyde, 16, 35; propanal, 7, 14; *n*-butanal, 2, 6.6; benzaldehyde, 0.5, 1.0.

Composition of aldehydes in ambient air in the South Coast Air Basin. The composition of aldehydes in ambient air samples can be estimated from samples analyzed concurrently for total aldehydes and individual aldehydes. Partial composition relationships can be obtained from some of the other studies.

The measurements obtained by Renzetti and Bryan (1961) using the bisulfite method resulted in collection of ketones but at low collection efficiency (Wilson, 1958). Therefore, the percentages of formaldehyde and acrolein as calculated are underestimated in terms of aldehydes only. The average compositions in percentages are as follows: Downtown Los Angeles, formaldehyde, 49; acrolein, 4; South Pasadena, formaldehyde, 28; acrolein, 6.

The following year formaldehyde, acrolein and total aldehydes were determined by spectrophotometric methods (Altschuller and McPherson, 1963). Based on these results the average composition from the samples collected in downtown Los Angeles was as follows: formaldehyde, 48, acrolein, 20. However, only a small number of samples were analyzed by all three spectrophotometric methods. In a larger subset with concurrent formaldehyde and acrolein measurements, the acrolein concentration was 20% of the formaldehyde concentration. From the measurements by these same three methods made in October 1968 (Scott Research Laboratories, 1969), the average composition in percentages are as follows: Huntington Park, CA, formaldehyde, 45; acrolein, 4: El Monte, CA, formaldehyde, 56; acrolein, 5.

As discussed earlier, Grosjean (1982) and Grosjean and Kok (1981) reported a group of HPLC measurements of a number of aldehydes at the Harvey Mudd College site in Claremont, CA. Concentrations were measured for formaldehyde and four other aldehydes. The average composition can be calculated from the subset of samples in which the four saturated aldehydes were above detectability limits. The average composition computed based on this group of aldehydes is as follows: formaldehyde, 55; acetaldehyde, 25; propanal, 16; *n*-butanal, 3; benzaldehyde, 1. The composition of individual samples varied widely. There are a few samples in which the acetaldehyde or propanal concentrations were reported to equal or exceed the formaldehyde concentration. On the other hand, in some of the samples the formaldehyde concentration substantially exceeded the sum of concentrations of all of the other aldehydes. The ketone, 2-butanone, also was measured in many of the samples taken at the Harvey Mudd College site in Claremont, CA (Grosjean, 1982).

Trends in aldehydes and in formaldehyde concentrations in the South Coast Air Basin. Considerable care is necessary in evaluating the available results for indications of aldehyde trends and in formaldehyde concentrations. Comparisons are complicated by a number of factors including (1) the short duration of measurement in many studies, (2) selection of sampling sites, (3) differences in analytical methods used and (4) year to year meterological variations.

Average 'aldehyde' concentrations during the period of measurement ranged from 30 to 150 ppb at the various sites utilized within Los Angeles County from 1954 to 1957 (Dickerson, 1961). The average concentrations obtained from the three studies carried out during the 1960s ranged from 50 to 150 ppb (Altshuller and McPherson, 1963; Renzetti and Bryan, 1961; Scott Research Laboratories, 1969). In the study located at Harvey Mudd College in Claremont, CA in 1980, the average concentration of carbonyls was 54 ppb

(Grosjean and Kok, 1981). Based on these results alone it is not possible to demonstrate any trend in total aldehyde concentrations. Evaluating trends of aldehydes is complicated both by the variations in analytical methods as well as the use of different sites in the various studies.

The intercomparison studies on analytical methods discussed earlier in this section do show reasonably good agreement particularly in terms of average formaldehyde concentrations over the same measurement periods between the chromotropic acid method and high performance liquid chromatography (Grosjean and Kok, 1981; Singh *et al.*, 1982). However, comparisons of these methods with LP-FTIR is complicated by the much shorter sampling period used in the LP-FTIR analysis (Hanst *et al.*, 1982).

One of the most critical limitations in evaluating trends of formaldehyde concentrations in the South Coast Air Basin is the selection of sampling sites over the years. In the earlier studies the sites used were in a western portion of the South Coast Air Basin in downtown Los Angeles and sites within 8–16 km of downtown Los Angeles. None of the earlier sampling for formaldehyde and other aldehydes was carried out in Claremont, CA or Riverside, CA. In contrast, most of the recent sampling has been carried out at sites in eastern areas of the Basin in Claremont, CA or Riverside, CA. The only site used in recent studies which is reasonably close geographically to the sites used earlier is the site at California State University in the eastern part of the City of Los Angeles.

The average concentrations of formaldehyde measured by HPLC and by the CA method, (Grosjean and Kok, 1981) of about 20 ppb at the California State University site (Table 5) are substantially lower than the average formaldehyde concentrations of 30–70 ppb measured in the 1960s in this area of the Basin. In contrast, the average formaldehyde concentration measured by LP-FTIR at the California State University site in June 1980 of 44 ppb (Grosjean and Kok, 1981; Hanst *et al.*, 1982) falls within the range of average formaldehyde concentrations from measurements made during the 1960s.

The measurements of lower concentrations of formaldehyde in recent years at sites in the eastern part of the Basin compared to higher concentrations of formaldehyde in earlier studies carried out at sites in the western part of the Basin cannot be used directly to determine a trend with time. However, an indirect approach is available.

An evaluation has been made of the trends in HC concentrations in the South Coast Air Basin area (Trijonis and Mortimer, 1982). As discussed earlier in this review, formaldehyde and other aldehydes are formed in the atmosphere from reactions involving HCs and yields of aldehyde are proportional to HC concentrations. Therefore, HC trends should be useful as a surrogate of trends in aldehydes. Aldehydes also are formed through incomplete combustion and are emitted directly from sources such as motor vehicles. HC measurements also may be a useful surrogate for trends in emissions of aldehydes from motor vehicles. The trends computed in the South Coast Air Basin area based on either emissions of HCs or on ambient HC concentrations are in good agreement (Trijonis and Mortimer, 1982). In downtown Los Angeles the average of percentage changes of HCs from contributing emission areas between 1965 and 1977 was −24 percent, while in areas further east such as Azusa and San Bernandino the average of percentage changes from contributing emission areas between 1965 and 1977 was −14 percent. If the HCs do serve as adequate surrogates for aldehydes, these results would be consistent with a moderate downward trend in aldehyde concentrations in the Basin.

Assuming that the HC trends do serve as surrogates for the aldehyde trends, the computations by Trijonis and Mortimer (1982) can be used to adjust the formaldehyde concentrations in the 1960s in and around downtown Los Angeles to what the formaldehyde concentrations might have been in the late 1970s. Applying the 24% decrease discussed above would still result in formaldehyde concentrations in the western part of the Basin being higher in the late 1970s than the concentrations measured at sites in the eastern part of the Basin such as Claremont, CA and Riverside, CA. This estimate is consistent with the indications based on the LP-FTIR measurements of a downward gradient in formaldehyde concentrations from west to east in the Basin.

Measurements of total aldehydes in other urban areas within the United States. The concentration of aldehydes also has been measured in several other urban areas. Aldehydes were measured at four sites in Houston, Texas during 1978 by use of the MBTH method (Table 5). Samples were collected during the morning and the early afternoon (Joshi, 1979; Nitz and Martinez, 1982). Aldehydes have been measured by the MBTH method during daylight at three sites in Columbus, OH during 1980. Results are given in Table 5 at only two sites, because of the very limited number of measurements reported for the third site (Joshi *et al.*, 1981). The MBTH method also was used to measure aldehydes at two sites in Atlanta, GA during 1981 (Corse, 1981). The samples in all three studies were collected over 2- to 3-h periods.

The 24-h average MBTH procedure (Hauser and Cummins, 1964) was used to obtain samples at up to 43 sites in the Gulf Coast area of Texas. The results have been evaluated for the years 1973, 1974 and 1975 (Jeffries and Kamens, 1978). Arithmetic mean values usually ranged between 4 and 16 ppb. In 1974, the average across all sites was 6.3 ppb. The highest 24-h average values for 1973, 1974 and 1975 were 25, 24 and 38 ppb. This procedure also was used at 12 sites in the Cincinnati, OH area in 1973, 1974 and 1975 (Jeffries and Kamens, 1978). The annual mean values averaged over all sites in the Cincinnati, OH area in 1973, 1974

and 1975 were 9, 10 and 11 ppb. The highest 24-h average aldehyde values in the Cincinnati area for the 3 years were 35, 65 and 29 ppb. Results by this same procedure also were available for samples collected every fourth day for St. Paul, MN for 1974. The annual mean concentration in 1974 averaged 10 ppb with a highest 24-h average value of 49 ppb.

The total aldehyde concentrations measured in these urban areas fall at or below the lower end of the range of aldehyde concentrations measured within the South Coast Air Basin area (Table 5).

Measurements of formaldehyde and acetaldehyde in other urban areas within the United States. Cleveland *et al.* (1977) carried out a statistical analysis of formaldehyde measurements made by the New Jersey Department of Environmental Health at sites in Bayonne, NJ, Camden, NJ, Elizabeth, NJ and Newark, NJ. The analyses were obtained by use of automated colorimetric analyzers using a modification of the Schiff's test for aldehydes, (Lyles *et al.*, 1965). The method is essentially specific to formaldehyde. The median and upper decile daily averages reported for formaldehyde in ppb during the period between 1 May and 30 September 1974 were as follows: Bayonne, NJ, 6.1, 9.5; Camden, NJ, 3.8, 7.0; Elizabeth, NJ, 5.5, 10.0; Newark, NJ, 6.6, 10.3. A decrease in formaldehyde concentrations from weekdays to Saturdays to Sundays was associated with traffic flows (Cleveland *et al.*, 1977). On the group of days with sufficient photochemical activity to produce O_3 concentrations above 100 ppb, the diurnal formadehyde concentrations were two to three times as high as on days when the O_3 concentrations were equal to or less than 50 ppb. Maximum formaldehyde concentrations were at Bayonne, NJ and Newark, NJ and occurred in the late morning and early afternoon, while the maximum O_3 concentrations occurred several hours later in the day.

Formaldehyde was measured at four sites in and around Houston, TX in September–October 1978 (Joshi, 1979). Collection was in a chromotropic acid solution in sulfuric acid. The average and maximum concentrations obtained are listed in Table 5.

In a study in Atlanta, GA during 1981 formaldehyde was measured by both the chromotropic acid method and by high performance liquid chromatography (Corse, 1981). Blank corrections for the HPLC measurements were not obtained. The average and maximum concentrations of formaldehyde listed in Table 5 are those obtained by use of the chromotropic acid method.

In Columbus, OH during July and August 1980, measurements for formaldehyde were made primarily by HPLC with a limited number of measurements made by use of the chromotropic acid method (Joshi *et al.*, 1981). The average and maximum formaldehyde concentrations listed in Table 5 for the two sampling sites are those obtained by use of high performance liquid chromatography.

Singh *et al.*, (1982) used the CA method to obtain formaldehyde concentrations in urban areas across the United States during 1–2 week periods in 1980 and 1981. The average and maximum concentrations in ppb at these sites were as follows: Denver, CO, 12.3, 28.7; St. Louis, MO, 11.3, 18.7; Chicago, IL, 12.8, 17.2; Pittsburgh, PA, 20.6, 35.1; Staten Island, NY, 14.3, 45.9.

The average and maximum formaldehyde concentrations measured in several of these urban areas fall within the range of formaldehyde concentrations measured at the sites in the eastern parts of the South Coast Air Basin. Therefore, there is an overlap in formaldehyde concentrations measured in urban areas elsewhere in the United States with the concentrations in the South Coast Air Basin.

Measurements of acetaldehyde were made by high performance liquid chromatography at sites in several midwestern cities (Joshi *et al.*, 1981; Singh *et al.*, 1982). The average and maximum concentrations, in ppb, for acetaldehyde by site and year are as follows: Fort Hayes, Columbus, OH, 1980, 2.1, 6.5; WVCO, Columbus, OH, 1980, 0.7, 1.6; Pittsburg, PA, 1981, 1.4, 2.6; Chicago, IL, 1981, 2.1, 3.4. These concentrations of acetaldehyde are substantial lower than those reported for sites within the South Coast Air Basin area (Grosjean, 1982; Grosjean and Kok, 1981).

Measurement of formaldehyde at nonurban sites in the United States. Formaldehyde has been collected in water vapor condensed onto a cooled surface and analyzed colorimetrically (Farmer and Dawson, 1982). This technique was applied at a rural site 56 km west of Tucson, AZ during July–August 1981. Most of the formaldehyde concentrations obtained were in the 0.1–0.8 ppb range.

Measurements of formaldehyde at locations outside of the United States. Neitzert and Seiler (1981) measured formaldehyde by use of cryogenic preconcentration followed by electron capture gas chromatographic analysis of formaldehyde as its 2,4-dinitrophenylhydrazone. At Finthen, about 8 km west of Mainz, W Germany, the formaldehyde concentrations measured from July to October 1979 ranged from 0.7 to 5.1 ppb with a mean value of 1.9 ppb.

Platt *et al.* (1979) and Platt and Perner (1980) measured formaldehyde by use of long path differential ultraviolet absorption spectroscopy in and near the town of Jüluch between Aachen and Cologne, West Germany from May to October 1978. The formaldehyde concentrations measured ranged from 0.1 ppb up to 6.5 ppb and averaged about 2 ppb. These authors noted that the site could be impacted by pollutants transported from adjacent industrial areas. At a rural site 40 km from Jüluch the formaldehyde concentration measured in October 1978 averaged about 1 ppb. Lowe *et al.* (1980) measured formaldehyde by use of high performance liquid chromatography at Jüluch from August 1979 to May 1980. During this period formaldehyde concentrations ranged from 0.3 to 4.5 ppb.

Both Platt and Perner (1980) and Neitzert and Seiler (1981) reported formaldehyde measurements at Deuselbach in the Hunsrueck Mountains of West Germany. Platt and Perner (1980) measured formaldehyde concentrations ranging from < 0.03 to 0.9 ppb during April 1979. Neitzert and Seiler (1981) during November 1979 reported higher concentrations of formaldehyde than obtained by Platt and Perner (1980). These latter investigators obtained formaldehyde concentrations ranging from 0.4 to 3.8 ppb and averaging 1.7 ppb.

The earlier unpublished measurements obtained by Hadamczik (1947) at several sites in central Europe are cited by Platt *et al.* (1979). Hadamczik reported formaldehyde concentrations ranging from 0 to 5.5 ppb in 1941–1944.

Lowe *et al.* (1980) measured formaldehyde by HPLC on aircraft samples taken over West Germany. At altitudes at and below 3 km, the concentrations of formaldehyde measured ranged from 0.18 to 0.54 ppb averaging 0.34 ppb.

Yokouchi *et al.* (1979) measured concentrations of formaldehyde up to 10 ppb at Tsukdaba, Japan. These investigators collected samples of air in tubes packed with molecular sieve 13 ×, removed water and analyzed for formaldehyde by gas chromatographic–mass spectrometric analysis.

Several investigators have measured formaldehyde in maritime air masses. Platt *et al.* (1979) and Platt and Perner (1980) measured formaldehyde concentrations of about 0.2 ppb in maritime air at Dagebull on the north coast of West Germany in October 1979. These investigators also measured formaldehyde at Loop Head on the west coast of Ireland (Platt and Perner, 1980). At this site, formaldehyde concentrations were below the detectability limits ranging from 0.07 to 0.3 ppb. Neitzert and Seiler (1979) measured formaldehyde at Cape Point, South Africa in December, 1979. The formaldehyde concentrations ranged from 0.2 to 1 ppb averaging 0.5 ppb. Zafiriou *et al.* (1980) measured formaldehyde at a site on Sand Island, Eniwetok Atoll, Marshall Islands during June and July 1979. The formaldehyde concentrations obtained after cryogenic preconcentration by use of colorimetric analyses ranged from 0.11 to 0.57 ppb and averaged 0.4 ppb.

Measurements of formaldehyde were made during cruises on research vessels in the western North Pacific during April–May 1975 and in the western North Pacific to the eastern Indian Ocean (Fushima and Miyake, 1980). Analyses were made by the CA and MBTH colorimetric methods. The formaldehyde concentrations measured ranged from < 0.8 to 9 ppb. Almost 2/3s of the formaldehyde concentrations reported exceeded 2 ppb. These concentrations are substantially larger than reported by the other investigators (Neitzert and Seiler, 1979; Platt *et al.*, 1979; Platt and Perner, 1980; Zafiriou *et al.*, 1980) in maritime air.

The formaldehyde concentrations reported at continental sites in Europe are well below these usually measured in the United States. However, the European measurements were made at nonurban sites while those in the United States usually were made well within urban areas. The formaldehyde concentrations in maritime air, excepting the results of Fushima and Miyoke (1980), averaged at or below 0.5 ppb. The maritime background concentration appears to be a factor of 10 to 100 below the formaldehyde concentration within urban areas.

Formaldehyde and aldehydes as percentages of concurrently measured oxidant or ozone concentrations. In Tables 4 and 5 values of (formaldehyde/oxidant or O_3) × 100 and of (aldehydes/oxidant or O_3) × 100 are tabulated. O_3 has a rapid increase to maximum value during daylight hours followed by a rapid decrease into the evening. Aldehydes show a less pronounced maximum than O_3 usually somewhat earlier in the day. Aldehydes do not drop off as rapidly as does O_3 at night. As a result, formaldehyde and aldehyde concentrations tend to be a larger percentage of O_3 or oxidant concentrations during daylight or daylight and evening than at times when O_3 or oxidant are at their maximum concentrations. The differences in percentage can be a factor of 2 or more. For example, at Claremont, CA in 1978, formaldehyde concentrations were 30% of O_3 concentrations over all hours of measurement, but 13% at the times of maximum O_3 concentration.

The formaldehyde concentrations as a percentage of the O_3 concentration can vary by factors of as much as 2 to 3 on different days during the same study (Tuazon *et al.*, 1980, 1981a). Similarly, factors of 2 or 3 in the percentage the formaldehyde concentration is of the O_3 concentration can occur from year to year in the averages at the same time of different locations within the same area (Tuazon *et al.*, 1978, 1980, 1981b).

In the measurements made during the 1955–1957 period in Los Angeles County, (Table 4), the aldehyde concentrations exceeded the oxidant concentrations in some years at a number of sites (Dickerson, 1961). Measurements during later years do not indicate aldehyde concentrations reaching as high a percentage of concurrent oxidant or O_3 concentrations as do the measurements during the 1950s in Los Angeles. In more recent studies the aldehydes were as high as 50% or more of the concurrent average oxidant or O_3 concentrations, (Grosjean and Kok, 1981; Hanst *et al.*, 1982). Formaldehyde concentrations in a number of studies ranged from 15 to 30% of average oxidant in O_3 concentrations although both higher and lower percentages have been reported.

Formaldehyde concentrations as average percentages of oxidant or O_3 concentrations are usually higher in the western part, 25–100 + %, compared to the eastern part of the South Coast Air Basin, 5–30% (Table 5). Such results would be consistent with a higher density of mobile and stationary source combustion emissions in the western part of the South Coast Air Basin. Since formaldehyde formation is not

inhibited in the morning by NO as is O_3 and PAN, it can build up rapidly in the morning in areas with high emission densities.

Formaldehyde and aldehyde concentrations also are a significant percentage of O_3 concentrations at sites in Houston, TX, Columbus, OH and Atlanta, GA (Table 5). At the downtown and higher emissions sites in Houston, TX, as in the South Coast Air Basin area, aldehyde concentrations are a higher percentage of O_3 concentrations than at residential or suburban sites.

Long path ultraviolet measurements provide concurrent concentrations for O_3 and formaldehyde at Jüluch, West Germany (Platt *et al.*, 1979). Averaged over all the concurrent measurements, the formaldehyde concentration was 8% of the O_3 concentration at this site. This value is near the lower end of the range of percentages computed from the measurement at the sites in the United States.

4.2. *Formic acid*

The formation of formic acid in atmospheric mixtures has been shown under laboratory conditions to result from the reaction of formaldehyde with HO_2 radicals. Detailed experimental results supporting this mechanism have been reported (Su *et al.*, 1979; Veyret *et al.*, 1982). Veyret *et al.* (1982) computed for polluted atmospheres with HO_2 concentrations of 10^9 cm^{-3} that the reaction of HO_2 radical with formaldehyde to produce formic acid should be close to 30% of the total chemical removal rate of formaldehyde.

Ambient air measurements of formic acid in the South Coast Air Basin. In 1973 formic acid was measured in Pasadena, CA by LP-FTIR utilizing the distinctively shaped band centered at 1105 cm^{-1} (Hanst *et al.*, 1975). The maximum concentration of formic acid during the 24–26 July 1973 period of measurement was 19 ppb. This value for formic acid is based on the newer absorption coefficient (Hanst *et al.*, 1982; Tuazon *et al.*, 1981a, b). The detection limit for formic acid was 2 ppb.

Formic acid measurements by LP-FTIR were reported for the Riverside, CA site in 1976 and 1977 (Tuazon *et al.*, 1978, 1980, 1981a,b) at Claremont in 1978 (Tuazon *et al.*, 1981b) and at California State University within the city of Los Angeles in 1980 (Hanst *et al.*, 1982). The average and maximum formic acid concentration in ppb by year are as follows: 1976, 2, 7; 1977, 5, 13; 1978, 6, 19 and 1980, 4, 10.

The ratios of formic acid to formaldehyde at the time of peak formaldehyde concentrations are as follows: Riverside, 1976, 0.22; Riverside, 1977, 0.26; Claremont, 1978, 0.20; California State University, 1980, 0.15. The overall average ratio from the measurements at these three sites is 0.23 with 90% of the daily values within the range 0.23 ± 0.1. Averaging over all of the individual concentration values for the four studies results in a ratio of 0.3.

Although formic acid peaked at the same time that O_3 did on a number of days of measurement in the LP-FTIR measurements, on several other days formic acid peaked 1 to 2 h later in the afternoon (Hanst *et al.*, 1975, 1982; Tuazon *et al.*, 1978, 1980, 1981a,b). At the peak in O_3 concentration, the formic acid concentrations ranged from 1 to 4 per cent of the O_3 concentrations. Formic acid as a percentage of O_3 at the time of peak O_3 concentration varied from day to day by factors of as much as 4 to 5 (Tuazon *et al.*, 1980, 1981b).

Ambient air measurements of formic acid at rural remote sites in the United States. Formic acid has been measured at several other sites in the SW United States by a technique involving collection on a film of water followed by ion chromatography (Dawson *et al.*, 1980). At a site 16 km NW of Tucson, AZ formic acid concentrations in the 1.5–3.5 ppb range were reported during December 1979. At relatively remote sites, Saguno National Monument, AZ and on the Papapo Indian Reservation, AZ formic acid concentrations in January–February 1980 ranged from ~0.5 to 1.5 ppb. Farmer and Dawson (1982) measured formic acid concentrations between a few tenths of a ppb and 3 ppb at a site 56 km SE of Tucson, AZ during July–August 1981.

4.3. *Peroxyacyl nitrates (PANs)*

Atmospheric chemistry. There are a number of similarities in the atmospheric formation of O_3 and PANs. Both are dependent on the prior formation of a precursor, NO_2, and their formation is inhibited until NO is converted to NO_2. Their formation is dependent on the availability of HO_2, RO_2, $RC(O)_2$ radicals to convert NO to NO_2 (see references in Introduction). Since formation of these radicals is largely dependent on available sunlight, O_3 and PAN formation rates should be very small early in the morning and increase slowly during the morning. The formation of O_3 and PAN will tend to be fast in the middle of the day. By the early evening, diminished solar radiation will reduce the rate of the photolysis of NO_2 to form O atoms needed to form O_3. Similarly, the formation of $RC(O)O_2$ radicals depends on the reaction of OH radicals with aldehydes, and the rate of formation of OH radicals will slow up as solar radiation diminishes (see references in Introduction). However, while O_3 reacts rapidly in the late afternoon and evening with freshly emitted NO, the reaction of PAN with NO is much slower. The dry deposition velocity of PAN is lower than that of O_3 (Garland and Penkett, 1976).

Methods of measurements. PANs were first identified in laboratory studies and subsequently in the atmosphere of Los Angeles by use of long path infrared spectroscopy (Scott *et al.*, 1957; Stephens *et al.*, 1956a,b, 1961). Subsequent development and application of Fourier transform infrared spectroscopy with infrared long path cells substantially increased the sensitivity of infrared methods (Hanst, 1982; Hanst *et al.*, 1971, 1975; Tuazon *et al.*, 1978). The improved long path Fourier transform infrared system was operated

at a pathlength of 900 m and a resolution of 0.5 cm^{-1} with a detection limit for PAN of 3 ppb (Tuazon *et al.*, 1981b). The 1162 cm^{-1} band has been used to monitor the ambient air concentrations of PAN.

The first use of electron capture detectors with gas liquid partition chromatography to measure PANs was reported by Darley *et al.* (1963). PAN and peroxypropionyl nitrate (PPN) were separated and analysed. Detectability limits of 0.1–0.2 ppb have been reported (Jorgen, 1978; Kopczynski *et al.*, 1972; Spicer, 1977). Singh *et al.* 1979, 1981 obtained lower detectability limits by preconcentration.

Both long path infrared spectroscopy and electron capture gas chromatography have been used to obtain PAN concentrations in the South Coast Air Basin area. Measurements of PAN elsewhere in the United States and in other countries have been obtained by use of electron capture gas chromatography.

Measurements of PAN in the South Coast Air Basin. The average and maximum concentrations of PAN measured in the South Coast Air Basin area are summarized in Table 6. When concurrent measurements of O_3 or oxidant were available, the percentages, (PAN/O_3 or O_3) × 100 were computed and also are tabulated in Table 6 from the concentrations averaged over an entire study and the times of maximum O_3 or oxidant concentrations each day during a study.

The highest average and maximum concentrations of PAN have been measured within the city of Los Angeles and at other locations in the western part of the South Coast Air Basin (Table 6). Concentrations of PAN measured within Riverside, CA and other locations in the eastern part of the South Coast Air Basin also are higher than PAN concentrations measured in most other urban areas in the United States.

In downtown Los Angeles, CA, Mayrsohn and Brooks (1965) measured maximum concentrations of PAN between 1000 and 1300 h. In Pasadena, CA, Hanst *et al.* (1975) reported that the maximum PAN concentrations occurred between 1000 and 1500 h. Further east in West Covina, the time at which the peak in PAN concentration occurred averaged over the study near 1400 h (Spicer, 1977). Even further east in the South Coast Air Basin at Claremont, measurements in 1978–1979 indicated that the maximum PAN concentrations occurred betwen 1500 and 1800 h (Tuazon, 1981a,b). At the same site in Claremont during 1980, Grosjean and Kok (1531) obtained maximum diurnal concentrations of PAN between 1530 and 2050 h, but most frequently between 1500 and 1700 h. Therefore, consistent with the wind movements in the South Coast Air Basin the times at which maximum PAN concentrations occur shift to later in the afternoon for locations further east in the Basin area.

Continuing measurements for PAN were made in Riverside, CA from May 1975 to October 1976 by Pitts and Grosjean (1979). Averaged diurnal curves were plotted for three time periods: May–October 1975; November 1975–April 1976; May–October 1976. Two peaks occurred in the diurnal measurements of concentrations of PAN at this site. The earlier PAN maximum and the later and higher maximum in PAN concentrations occurred during the following time periods; May–October 1975, 1100 and 1500 h; November 1975–April 1976, 1300 and 1700 h; May 1976, 1200 and 1600 h. The earlier peaks observed can

Table 6. Ambient air measurements of peroxyacetyl nitrate concentrations at urban and suburban sites in the United States

Site/Ref. (Method)	Period of year No. of days	Period of day	Peroxyacetyl nitrate, ppb Av.	Max.	(PAN/O_3) × 100 Av.	at O_3 10, peak
Downtown Los Angeles, CA Renzetti and Bryan (1961) (IR)	July–Oct. 1960 (9)	0900–1200	~20*	70	8	7
Downtown Los Angeles, CA Mayrsohn and Brooks (1965) (EC-GC)	Sept.–Oct. 1965 (35)	0800–1300	31	214	NA†	7
Downtown Los Angeles, CA Lonneman *et al.* (1976) (EC-GC)	Sept.–Nov. 1968 (NA)†	1000–1600	8	68	13	NA†
W. Los Angeles, CA Hanst *et al.* (1982) (LP-FTIR)	June 1980 (2)	0635–1335	7	16	9	6
Pasadena, CA Hanst *et al.* (1975) (LP-FTIR)	July 1973 (3)	0700–1630	30	53	10	8

Table 6. (Contd)

Site/Ref. (Method)	Period of year No. of days	Period of day	Peroxyacetyl nitrate, ppb Av.	Max.	$(PAN/O_3) \times 100$ Av.	at O_3 10, peak
West Covina, CA Spicer (1977) (EC-GC)	Aug.–Sept. 1973 (24)	23 h	9	20	20	12
Claremont, CA Tuazon *et al.* (1981a, b) (LP-FTIR)	Oct. 1978 (5)	late morning to late evening	6	11	7	6
Claremont, CA Tuazon *et al.* (1981a) (EC-GC)	Aug.–Sept. 1979 (8)	morning to late evening	4	11	4	4
Claremont, CA Grosjean and Kok (1981) (EC-GC)	Sept.–Oct. 1980 (11)	24 h	13	47	NA†	NA†
Riverside, CA Taylor (1969) (EC-GC)	Aug. 1967–April 1968 (273)	24 h	3.8	58	8	NA†
Riverside, CA Pitts and Grosjean (1979) (EC-GC)	May 1975–Oct. 1976 (533)	24 h	3.6	32	9	5
Riverside, CA Tuazon *et al.* (1978) (LP-FTIR)	Oct. 1976 (3)	late morning early evening	9	18	5	4
Riverside, CA Tuazon *et al.* (1980) (LP-FTIR)	July Aug., Oct. 1977 (10)	late morning to evening	7	18	4	4
Riverside, CA Singh *et al.* (1979) (EC-GC)	April–May 1977 (10)	24 h	1.6	5.7	4	NA†
Riverside, CA Temple and Taylor (1983) (EC-GC)	Jan.–Dec. 1980 (365)	0800–2000	4.9	41.6	NA†	NA†
Houston, TX (Lange) Westberg *et al.* (1978) (EC-GC)	July 1976 (22)	24 h	0.4	11.5	3	3
St. Louis, MO Lonneman *et al.* (1976) (EC-GC)	June–Aug. 1973 (12)	8–24 h	6.3	25	13	NA†
St. Louis, MO Spicer (1977) (EC-GC)	July–Aug. 1973 (26)	23 h	1.8	19	5	5
Dayton, OH (Huber Hts) Spicer *et al.* (1976) (EC-GC)	July–Aug. 1974 (20)	24 h	0.7	10	2	1
Hoboken, NJ Lonneman *et al.* (1976) (EC-GC)	June–Aug. 1970 (NA)†	1000–1600	3.7	9.5	4	NA‡
New Brunswick, NJ (Cook college) Brennan (1980) (EC-GC)	25 Sept 1978–16 May 1980 (600)	24 h	0.5	10.6	4	2

* Approximate value.
† Not available.

be associated with local emissions. However, the later and higher afternoon maximum in PAN concentrations appeared to be associated with PAN and other products formed by reactions of precursors in air masses moved from west to east by onshore winds during the afternoon.

The times of maximum PAN concentration occur during the same part of the day and frequently during the same hour of the day as do the maximum concentration of O_3 at sites in the South Coast Air Basin (Pitts and Grosjean, 1979; Spicer, 1977; Taylor, 1969; Temple and Taylor, 1983; Tuazon *et al.*, 1981a,b). In Riverside, CA and Claremont, CA the measurements made by LP-FTIR and by electron capture gas chromatography in 1979 resulted in maximum PAN and O_3 concentrations occurring within 30 min of each other on 90 per cent of the days (Tuazon *et al.*, 1978, 1980, 1981a,b).

In Riverside, CA the measurements of O_3 indicated an inflection in the O_3 diurnal curve earlier in the day and a maximum later in the day (Pitts and Grosjean, 1979). The maximum in the O_3 concentration occurred at the same time as the maximum in the PAN concentration during the period from May 19 to October 1975. During the November 1975–April 1976 and May 19–October 1976 periods in Riverside, CA the maximum in O_3 concentration occurred 1 to 2 hrs earlier than the maximum in PAN concentrations (Pitts and Grosjean, 1979).

Taylor (1969) observed that PAN was more persistent than O_3 during the night and also during an extended period of air stagnation. Comparisons of diurnal curves for O_3 and PAN obtained during 1975–1976 in Riverside, CA show PAN to be more persistent than O_3 throughout the year (Pitts and Grosjean, 1979). While the O_3 concentrations decreased to very low values at night compared to the afternoon the PAN concentrations at night averaged 1/3 to 1/2 of afternoon PAN concentrations. At Claremont, CA (Grosjean, 1983; Tuazon, 1981a) and West Covina (Spicer, 1977), the PAN also is more persistent than O_3 at night.

The PAN measurements at Riverside are extensive enough to permit seasonal comparisons (Pitts and Grosjean, 1979; Taylor, 1969; Temple and Taylor, 1983). In 1967–1968, a large decrease in monthly averaged PAN concentrations occurred during the winter (December–February). In 1975–1976 there was some decrease in PAN concentrations during the winter, but not so much as in 1967–1968. Pitts and Grosjean commented on the fact that unlike O_3, high concentration levels of PAN were frequently encountered during the winter of 1975–1976. Temple and Taylor indicated that an occasional episode of elevated PAN concentrations were found in December and February, but more frequently in November both in 1967–1968 and in 1980.

Trends in peroxyacetyl nitrate concentration in the South Coast Air Basin. Comparisons of the monthly average measurements made in 1975–1976 (Pitts and Grosjean, 1979) with those made in 1967–1968 (Taylor, 1969) do not indicate any consistent trend at the Riverside site. In 1975–1976, the early wintertime PAN concentrations are higher than in 1967–1968, the late winter and early spring PAN concentrations are about the same during the two periods, while the summer and fall concentrations are lower than in 1967–1968. Temple and Taylor (1983) concluded that the average maximum PAN concentrations in 1980 were similar to those in 1967–1968. Consequently, these investigators felt that there was little change in air quality over this period with respect of PAN. Although the measurements are less extensive at sites in the western parts of the South Coast Air Basin, the available measurements suggest a possible downward trend between 1960 and 1980 in PAN concentrations in this part of the Basin (Table 6).

Measurements of PAN at other urban areas within the United States. Average and maximum concentrations of PAN at sites within several other urban areas also are tabulated in Table 6. These PAN concentrations also were used along with oxidant or O_3 concentrations to compute the percentages (PAN/O_x or O_3) × 100. When a study did not provide oxidant or O_3 measurements, the average and maximum PAN concentrations are given in the text.

Singh *et al.* (1979) measured in San Jose, CA during August 1978 average and maximum PAN concentrations of 0.9 and 1.3 ppb. In Oakland, CA in June and July 1979, average and maximum PAN concentrations of 0.4 and 1.9 ppb were obtained (Singh *et al.*, 1981).

At a site in Houston, TX the maximum PAN concentrations in July 1976 occurred between 1300 and 1600 h (Westberg *et al.*, 1978). In subsequent measurements at 3 sites in the Houston area in June to October 1977, maximum PAN concentrations were measured from late morning to early evening (HAOS, 1979; Jorgen, 1978). Concentrations below detection limits usually occurred from early evening to the late morning (Jorgen, 1978; Westberg *et al.*, 1978). Only infrequently were measurable concentrations of PAN observed during the night. The average and maximum PAN concentrations by site were as follows: Aldine, 0.9, 15.6; Crawford, 0.6, 10.3; Fuqua, 0.6, 12.4; West Hollow, 0.6, 9. Martinez *et al.* (1982) reported average and maximum PAN concentrations of 0.8 and 7.0 ppb at an additional site (Jack Rabbit) in the Houston area during 1978.

In St. Louis during July–August 1973, Spicer (1977) reported that the average time for the occurrence of maximum PAN concentrations was at 1300 h. PAN was more persistent than O_3 with significant PAN concentrations throughout the night.

The most extensive PAN measurements available in the eastern United States were obtained at a site in New Brunswick, NJ between September 1978 and May 1980 (Brennen, 1980). The monthly average diurnal curves showed maximum PAN concentrations be-

tween 1300 and 1500 h. Measurable PAN concentrations were obtained through the night. The highest concentrations were measured in the late summer and early fall. The monthly average maximum O_3 and oxidant concentrations usually occurred within 1 h earlier or later of the maximum PAN concentrations.

Singh *et al.* (1982) measured PAN concentrations at a number of urban sites outside of California for periods of 1 or 2 weeks during 1979, 1980 or 1981. The average and maximum PAN concentrations, in ppb, by site are as follows: Phoenix, AZ, 0.8, 3.7; Denver, CO, 0.4, 11.6; Houston, TX, 0.4, 4.4; St. Louis, MO, 0.3, 0.9; Chicago, IL, 0.4, 1.6; Pittsburgh, PA, 0.3, 0.6; Staten Island, NY, 0.7, 3.9. For the site in Phoenix diurnal patterns were reported indicating maximum concentrations occurring near noon with significant concentrations of PAN remaining through the night. The highest average PAN concentrations reported outside of California have been in St. Louis, MO and Hoboken, NJ (Table 6). At other urban locations outside of California the average concentrations of PAN have been below 1 ppb. However, the maximum concentrations reported often exceed 10 ppb overlapping the concentrations measured at locations in the South Coast Air Basin. Such concentration levels indicate occasional photochemical smog episodes in these areas, intense as those occurring in the South Coast Air Basin.

Peroxyacetyl Nitrate as a Percentage of Concurrent Ozone Concentrations at Urban Sites. PAN concentrations constitute a variable percentage of O_3/oxidant concentrations among sites both for the average concentrations as well as at the time of maximum O_3/oxidant concentrations (Table 6). From day to day at the same locations the PAN concentrations as a percentage of the O_3 concentrations can vary by factors of 2 to 3 and even more (Spicer, 1977; Tuazon et al., 1978, 1980, 1981a,b).

The values of $(PAN/O_3) \times 100$ obtained from studies conducted in the South Coast Air Basin tend to be somewhat lower for sites in the E part of the Basin, Claremont, CA and Riverside, CA than those further W. The $(PAN/O_3) \times 100$ values are higher based on average concentrations over the 24-h period than at the time of O_3/oxidant maximum. This result is consistent with the greater persistence of PAN than O_3 at night in the South Coast Air Basin discussed earlier. At locations elsewhere in the United States the values of $(PAN/O_3) \times 100$ usually are on the low end of the range of values obtained from measurements in the South Coast Air Basin (Table 6). An exception is the high percentage value reported by Lonneman *et al.* (1976) at a downtown site in St. Louis, MO.

Measurements of Peroxypropionyl Nitrate at Urban Sites in the United States. Average and maximum concentrations of PPN measured at urban sites are listed in Table 7. With two exceptions, the average PPN is reported as constituting $\sim 20 \pm 10\%$ of the average concentration of PAN (Table 7). The maximum PPN concentration constitutes a highly variable percentage of the maximum PAN concentration.

Measurements at nonurban sites in the United States. Measurements of PAN and PPN (Lonneman *et al.*, 1976; Singh *et al.*, 1979; Spicer and Sverdrup, 1981; Westberg et al., 1978) at rural and remote sites are tabulated in Table 8.

An average PAN concentration of 0.74 ppb was measured in east central Missouri, 42 km west of St. Louis during 2 weeks in February 1981 (Spicer *et al.*, 1983). An average PAN concentration of 0.46 was obtained at Huntington Lake, a rural site in NE Indiana during April 1981 (Spicer *et al.*, 1983). The average concentration of PAN at Beverly Airport, MA was about 2 ppb (Spicer *et al.*, 1982a). Both PAN and O_3 peaked at 1600 h and PAN concentration was about 4% of the O_3 concentration at this site (Spicer and Sverdrup, 1981).

The PAN concentrations were measured along with a number of other substances including O_3 in a study in the New Jersey Pine Barrens (Jackson Township) at Van Hiseville in the summer of 1979 (Spicer *et al.*, 1983; Spicer and Sverdrup, 1981). Based on the average diurnal profile the PAN concentration peaks at 1500 h at 1.3 ppb and decreases down to concentrations of 0.1–0.3 ppb at night. On the average, the PAN concentration was slightly over 1% of the O_3 concentration at the time of maximum O_3 concentration (Table 8).

The concentrations of PAN and PPN at all except the more remote sites overlap the lower end of the concentration range at urban sites outside of the South Coast Air Basin area. The lowest average PAN concentrations reported at remote sites of about 0.1 ppb are a factor of 3 or 4 lower than the lowest urban concentration reported (Table 6). The values of $(PAN/O_3) \times 100$ at these non-urban rural sites ususally are substantially lower than at urban sites (Tables 6 and 8).

Ambient air concentrations of PAN outside of the United States. Measurements of PAN concentrations during the period 26 June–November 1972 were obtained on the outskirts of Delft in The Netherlands (Nieboer and Van Ham, 1976). On 48 of the 130 days of measurement PAN exceeded the instrumental detection limits of 1 ppb at least for 1 h. During these days the PAN on the average reached its maximum concentrations at 1400 h, while O_3 peaked about 1 h later. As observed in the United States, PAN disappeared more slowly than O_3 at night. The percentage $(PAN/O_3) \times 100$ depended on wind sector. When the wind flow was from a highly industrialized area, the PAN averaged 7% of the O_3 concentration. When the wind flow was over adjacent rural areas, the PAN averaged 2% of the O_3, while when the flow was from the North Sea, over The Hague and Delft the PAN averaged 3% of the O_3. At the time of peak O_3 concentration, the PAN was about 2% of the O_3 concentration. These percentages

Table 7. Ambient air measurements of peroxypropionyl nitrate concentrations by electron capture gas chromatography at urban sites in the United States

Site/Ref.	Period of measurement (No. of days)	Period of day	Nitrate Av.	Nitrate Max.	(PPN/PAN) × 100 Av.	(PPN/PAN) × 100 Max.
Los Angeles, CA Singh *et al.* (1981)	April 1979 (13)	24 h	0.7	2.7	0.15	0.16
Riverside, CA Darley *et al.* (1963)	NA* (1)	NA*	NA*	6	NA*	0.12
Riverside, CA Singh *et al.* (1979)	April–May	24 h	0.3	1.8	0.21	0.32
Riverside, CA Singh *et al.* (1981)	July 1980 (13)	24 h	0.2	0.9	0.16	0.16
San Jose, CA Singh *et al.* (1979)	August 1978 (7)	24 h	0.08	0.13	0.08	0.10
Oakland, CA Singh *et al.* (1981)	June–July 1979 (13)	24 h	0.15	0.5	0.42	0.28
Phoenix, AZ Singh *et al.* (1981)	April–May (1979 (14)	24 h	0.09	0.33	0.12	0.09
Denver, CO Singh *et al.* (1982)	June 1980 (14)	24 h	0.05	0.32	0.10	0.03
Houston, TX Singh *et al.* (1982)	May 1980 (12)	24 h	0.11	0.63	0.25	0.14
St. Louis, MO Lonneman *et al.* (1976)	10 Aug., 1973 (1)	1000–1530	3.0	5.0	0.17	0.20
St. Louis, MO Singh *et al.* (1982)	May–June, 1980 (9)	24 h	0.66	0.25	0.23	0.28
Chicago, IL Singh *et al.* (1982)	April–May, 1981 (13)	24 h	0.05	0.13	0.12	0.08
Pittsburgh, PA Singh *et al.* (1982)	April 1981 (11)	24 h	0.05	0.07	0.17	0.10
Staten Island, NY Singh *et al.* (1982)	March–April (1981 (11)	24 h	0.20	3.1	0.27	0.80

* Not available.

are on the low end of the range of percentages in the South Coast Air Basin, but similar to those obtained in a number of urban areas in the United States (Table 6). Nieboer and Van Ham also observed that the PAN formation rates decreased with increasing wind speed between 0700 and 1400 h.

Penkett *et al.* (1975, 1977) measured PAN at Harwell in southern England. Measurements of PAN were reported for the period between November 1974 and October 1975. Concentrations of PAN were low with monthly average values ranging from 0.06 ppb in December and January up to 0.77 ppb in August. Maximum diurnal PAN concentrations also were low with the highest value of 1.18 ppb being obtained in August 1975. Measurements also were made in London where the average diurnal curve was displaced upward from Harwell with a peak between 2 and 3 ppb. The maximum values obtained were 8.9 ppb at Harwell and 16.1 ppb in London during August 1975. The PAN concentration peaked between 4 and 8 ppb on a number of days in London during August 1975. The concentrations of PAN in London were below those in Los Angeles (Table 6). However, the concentration levels of PAN in the summer of 1975 in London appears comparable to those in cities in the United States other than those in the South Coast Air Basin.

In Tokyo, Izumikawa *et al.* (1975) measured up to 31 ppb in central Tokyo and 8 ppb in suburban Tokyo in the summers of 1972 and 1973. Fukuda and Terakado (1974) reported up to 6.7 ppb in the fall of 1972 in Tokyo. The maximum value of 31 ppb for central Tokyo was comparable to maximum values obtained

Table 8. Measurements of peroxyacetyl nitrate, peroxypropionyl nitrate and ozone at non-urban remote sites in the United States

Site	Nature of site	Period of measurement (No. of days)	Period of day	Average concentrations PAN	PPN	O_3	Maximum concentrations PAN	PPN	O_3	$(PAN/O_3) \times 100$ Average
Mill Valley, CA*	maritime	Jan. 1977 (12)	24 h	0.30	0.04	38	0.83	0.11	0.55	0.8
Point Arena, CA*	clean–maritime	Aug–Sept. 1978 (7)	24 h	0.08	ND‖	ND‖	0.28	ND‖	ND‖	ND‖
Badger Pass, CA*	remote–high altitude	May 1977 (10)	24 h	0.13	0.05	46	0.22	0.09	54	0.3
Reese River, NV*	remote–high altitude	May 1977 (7)	24 h	0.11	0.04	39	0.26	0.09	56	0.3
Jetmore, KA*	rural–continental	June 1978 (7)	24 h	0.25	ND‖	31	0.52	ND‖	53	0.8
Sheldon Wildlife Reserve, TX†	rural–continental	October 1978 (9)	24 h	0.64	ND‖	47	2.8	ND‖	148	1.4
Wilmington, OH‡	rural–continental	August 1974 (9)	24 h	NA¶	ND‖	NA[r]	4.1	ND‖	107	NA¶
Van Hiseville, NJ§	rural–continental	July–Aug. 1979 (31)	24 h	0.50	ND‖	36	6.5	ND‖	161	1.4

* Singh *et al.* (1979).
† Westberg *et al.* (1978).
‡ Lonneman *et al.* (1976).
§ Spicer and Sverdrup (1981).
‖ Not determined.
¶ Measured, but results not given in reference.

at some sites in the South Coast Air Basin (Table 6).

Nielsen *et al.* (1981) have investigated the transport of PAN in polluted air in northern Europe. PAN was monitored from June to September 1980 at Ris, a rural location in Denmark. Measurements at Ris could be influenced by the urban plumes of Copenhagen, Denmark, or Malmö, Sweden. On several days episodes of moderately elevated PAN were observed with daytime maximum in PAN and O_3 associated with high solar irradiation and stagnant or recirculated air masses in the area. During another group of days the local conditions were unfavorable to PAN and O_3 formation, there was a high percentage of cloud cover but there were stable winds from the southwest and relatively high wind speeds. On these days the PAN concentrations reached their maximum concentrations at midnight, 2.8 and 3.5 ppb. These were higher PAN concentrations than experienced during periods when conditions were favorable to local syntheses of PAN. In other such episodes the wind directions were from the northwest. The elevated PAN concentrations during all such episodes were associated with long-range transport into southern Scandinavia. The PAN concentrations during these periods at the rural site were 2–6% of the corresponding O_3 concentrations.

4.4. *Nitric acid*

Atmospheric chemistry. In daylight, the reaction of NO_2 with hydroxyl radicals is rapid (see references in Section 1). At night, the reaction of NO_2 to form NO_3 and N_2O_5 with subsequent reaction of N_2O_5 with H_2O may be significant in forming HNO_3. Since HNO_3 formation, as O_3 formation, is dependent on the availability of NO_2, the two species might be expected to have similar diurnal characteristics. However, HNO_3 once formed is more stable with respect to chemical removal processes than O_3.

Methods of measurement. HNO_3 concentrations were first measured in the ambient atmosphere during the early 1970s (Spicer, 1977; Spicer *et al.*, 1976). In early measurements a colorimetric technique was used by Spicer (1977). However, this method lacks both sensitivity and specificity and has not been used in later studies. A coulometric method, based on a modification of a mass microcoulometric meter so it would respond to acid gases, also was developed (Spicer, 1977). The difference in signal before and after removal of HNO_3 by a nylon fiber packed trap was used to obtain the HNO_3 concentration. Measurements can be made several times an hour with a detection limit of about 2 ppb.

Nitric acid has been measured in the ambient atmosphere by use of a long path Fourier transform infrared system operated at a pathlength of 900 m and a resolution of 0.5 cm^{-1} at 896 cm^{-1} (Tuazon *et al.*, 1978, 1980, 1981a,b). The detection limit for HNO_3 is 6 ppb. HNO_3 has been measured in the ambient air by absorption on a tungstic acid surface, desorbed into carrier gas, and carried into a chemiluminescent NO_x instrument for analysis (Braman *et al.*, 1982; McClenny *et al.*, 1982). The detection limit is 0.07 ppb.

A tandem filter technique involving collection of nitric acid on *n*-butyl ammonium hydroxide impregnated cellulose filters after removal of particulate nitrate on Teflon filters has been used (Huebert and Lazrus, 1978). Appel *et al.* (1980, 1981) employed a similar tandem filter technique involving collection of HNO_3 on either NaCl-impregnated cellulose filters or nylon filters after removal of particulate nitrate on teflon prefilters. A gas diffusion denuder was utilized by Appel *et al.* (1981) to measure nitrates.

A denuder difference technique with a tandem filter sampling system was used by Shaw *et al.* (1982) to measure nitric acid and particulate nitrate. Nylon filters were used in the tandem filter assembly to remove nitric acid.

Ambient air measurements at urban sites in the United States. HNO_3 was measured by the coulometric technique described above at West Covina, CA and within St. Louis, MO (Spicer, 1977) and within and near Dayton, OH (Spicer *et al.*, 1976). The average and maximum concentrations during the study periods during the summers of 1973 and 1974 are given in Table 9. Several of the higher 1-h maximum concentrations reported for HNO_3 approach the 1-h maximum concentrations of the NO_x and of O_3. Such high values for HNO_3 are unusual and possibly suspect. The HNO_3 concentration profiles during daylight did not match those of O_3. HNO_3 concentrations decreased substantially at night relative to afternoon values, but not as much as did O_3.

Measurements of HNO_3 concentrations were obtained by use of long path Fourier transform infrared spectroscopy in Riverside, CA during 1976 and 1977 (Tuazon *et al.*, 1978, 1980), in Claremont, CA during 1978 and 1979 (Tuazon *et al.*, 1981a,b) and in Los Angeles, CA during 1980 (Hanst *et al.*, 1982). The average and maximum concentrations of HNO_3 are given in Table 9. HNO_3 also was measured at Claremont, CA by Appel *et al.* (1981). The concentrations of HNO_3 measured by the tandem filter technique and gas diffusion denuder technique tended to be higher than by concurrent LP-FTIR measurements. The difference was considered to possibly result from loss of particulate nitrate passing through the denuder (Appel *et al.*, 1981). The HNO_3 concentrations peaked at or slightly earlier than the O_3 concentrations at these sites (Fig. 2). The higher concentrations of HNO_3 measured in Claremont relative to those measured in Riverside have been attributed to the higher ammonia concentrations transported into the Riverside area. These higher ammonia concentrations shift the equilibrium in ambient air towards formation of ammonium nitrate aerosol (Tuazon *et al.*, 1978, 1980, 1981a,b). This topic will be considered in more detail later in this review when considering aerosol species.

An intercomparison study was carried out in

Table 9. Ambient air measurements of nitric acid concentrations at urban and suburban rural sites in the United States

Site/Ref. (method)	Period of year (No. of days)	Hours of day	Nitric acid, ppb Av.	Max.	$(HNO_3/O_3) \times 100$ Av.	at O_3 peak
West Los Angeles, CA (Cal. State Univ.) Hanst *et al.* (1982) (LP-FTIR)	June 1980 (2)	0635–1335	7	12	9	5
West Covina, CA Spicer (1977) (coulometry)	Aug.–Sept, 1973 (27)	23 h	3	40	7	6
Claremont, CA Tuazon *et al.* (1981b) (LP-FTIR)	Oct. 1978 (5)	late mornings to late evenings	16	49	17	10
Claremont, CA Tuazon *et al.* (1981a) (LP-FTIR)	Aug.–Sept. 1979 (8)	early mornings	8	22	8	7
Riverside, CA (Tuazon *et al.* (1978) (LP-FTIR)	Oct. 1976 (3)	late morning to early evenings	4	8	2	1
Riverside, CA Tuazon *et al.* (1980) (LP-FTIR)	July, Aug., Oct. 1977 (10)	late morning to evening	6	20	4	3
St. Louis, MO Spicer (1977) (coulometry)	July–Aug. 1973 (23)	23 h	3	(80)*	9	8
Dayton, OH (downtown) Spicer *et al.* (1976) (coulometry)	July–Aug. 1974 (11)	24 hs	6	(54)*	18	8
Dayton, OH (Huber Hts) Spicer *et al.* (1976) (coulometry)	July–Aug. 1974 (19)	24 h	1	15	2	1
New Carlisle, OH Spicer *et al.* (1976) (coulometry)	July–Aug. 1974 (19)	24 h	2	(45)*	4	3
Res. Tri. Park, NC McClenny *et al.* (1982) (tungstic acid method)	July–July 1980 (4)	24 h	0.8	1.3	2	1
Beverly Airport, MA Spicer *et al.* (1982a) (integrated filter collection)	July–Aug. 1978 (14)	24 h		2.2	2	NA†
Van Hiseville, NJ Spicer and Sverdrup (1981) (integrated filter collection)	July–Aug. 1979 (31)	24 h	< 0.8	1.2	< 2	1
Abbeville, LA Cadle *et al.* (1982) (filter techniques)	June–Aug. 1979 (76)	24 h	0.7	NA†	NA†	2

* Unusually high values.
† Not available.

Claremont, CA for 8 days in August and September 1979 involving ten different HNO_3 measurements methods (Forest *et al.*, 1982; Spicer *et al.*, 1982b). The median values obtained from the ten methods varied during the 8-day period from 1.85 to 37.05 μg^{-3}, 17–14.4 ppb (Spicer *et al.*, 1982b). The HNO_3 concentrations were found to be highly correlated with the concentrations of O_3 and PAN as well as with ambient temperature and solar intensity (Spicer *et al.*, 1982b). On the average, gaseous and articulate nitrate contributed about equally to the total inorganic nitrate measured.

The average HNO_3 concentrations reported in St. Louis, MO and Dayton, OH are in the lower end of concentration range in the South Coast Air Basin (Table 9).

Ambient air measurements at nonurban sites in the United States. Spicer *et al.* (1976) reported HNO_3 concentrations by the coulometric technique at sub-

urban and small town/rural sites (Huber Hts., OH and New Carlisle, OH) outside of Dayton, OH. There were several 1-h maximun. HNO_3 concentrations that appear questionable. Spicer and Sverdrup (1981) measured HNO_3 in the New Jersey Pine Barrens at Van Hiseville, NJ by a dual Teflon/Nylon filter procedure. The results of these studies are tabulated in Table 9.

Measurements of HNO_3 at a number of suburban and rural locations by the Teflon/Nylon filter technique and a differential filter technique were made by Cadle *et al.* (1982). The differential technique which was used in Abbeville, CA and Commerce City, CO, subsequently was found to overestimate the HNO_3 concentration. The average HNO_3 concentrations by site in ppb were as follows: Commerce City, CO, 0.84; Abbeville, LA, 0.72; Warren, MI, fall, 0.30, winter, 0.51, spring, 1.33; Luray, VA, 0.36.

Farmer and Dawson (1982) measured HNO_3 after condensation with water vapor on a cooled surface followed by ion chromatographic analysis at a rural site 56 km SE of Tucson, AZ. The HNO_3 concentrations ranged up to 2 ppb with many samples containing nitric acid at concentrations between 0.5 and 1.5 ppb.

HNO_3 measurements were made by a tandem filter technique in a small town in northern California, Pittsburg, CA (Appel *et al.*, 1980). The concentrations of HNO_3 measured during a 4-day period in February, 1979 ranged from 0.3 to 1.6 ppb and averaged 0.8 ppb.

A tandem filter technique and the dual catalyst chemiluminescent technique were used to make HNO_3 measurements at a suburban airport site, Beverly, MA, an adjacent power plant plume and in the urban plume of Boston, MA (Spicer *et al.*, 1982a). At the airport site the HNO_3 concentration over a 14-day period averaged 1.0 ppb. On one day the power plant plume and the urban plume 29 km downwind over the ocean were measured to contain 6 and 5 ppb, respectively, of HNO_3.

Measurements of HNO_3 concentrations were made by both the tungstic acid integrated sampling method (McClenny *et al.*, 1982) and by a denuder difference technique with tandem filters (Shaw *et al.*, 1982) at a site in the Research Triangle Park, NC. During June, July and August, 1980 the 23-average concentrations of HNO_3 ranged from 0.1 to 1.5 ppb by the denuder difference technique. Concurrent measurements of HNO_3 were made by the tungstic acid integration sampling method (Table 9). Comparing the two methods by averaging over 23-h time periods on 2 days in July gave HNO_3 concentrations of 0.8 and 0.9 ppb by tungstic acid method and 0.9 and 0.8 ppb by the denuder difference technique (Shaw *et al.*, 1982). At a rural site at Croton, OH HNO_3 concentrations as measured by the tungstic acid method during August 1980 ranged from 0.2 to 1.4 ppb, except on one day when a peak of 3.8 ppb was attained (McClenny *et al.*, 1982).

Maximum HNO_3 concentrations were measured near midday with minimum values at night at Croton, OH (McClenny *et al.*, 1982). At Abbeville, LA the average diurnal profile had a maximum in concentration late in the morning with low concentrations at night (Cadle *et al.*, 1982). At Van Hiseville, NJ the average diurnal profiles showed that HNO_3 peaked in the middle of the afternoon and decreased to low concentrations at night (Spicer and Sverdrup, 1981). McClenny *et al.* (1982) did observe on some days that HNO_3 persisted well into the night.

HNO_3 was measured by a modification of the chemiluminescent NO_x monitoring technique at a rural site east of Boulder, CO (Kelly *et al.*, 1979). HNO_3 concentrations ranged from 0.5 to 5 ppb during measurements in February 1978 at this site. Kelly *et al.* (1980) subsequently measured HNO_3 at Niwot Ridge in the Rocky mountains between December 1978 and August 1979. In clean air the concentrations of HNO_3 frequently were below 0.03 ppb and ranged up to 0.1 ppb. In polluted air masses reaching this site HNO_3 concentrations ranged from 0.2 ppb upward with value above 1 ppb recorded occasionally.

Measurements at urban and rural sites outside of the United States. Measurements of HNO_3 have been made in Japan by use of a dual filter technique (Okita *et al.*, 1976). Within Tokyo during the period between 25 July and 30 August 1975 HNO_3 concentrations ranged from 0 to 2 ppb while in January 1976 the HNO_3 concentrations did not exceed 0.2 ppb. The HNO_3 concentration in the summer was about five times higher than in the winter in downtown Tokyo. Measurements also were made at Mt. Tsukaba about 80 km NNE of downtown Tokyo. During the period between 25 June and 3 July 1975 at Mt. Tsukuba the range of HNO_3 concentrations were about the same as in Tokyo. Additional measurements of HNO_3 at Mt. Tsukuba in October 1975 showed a decrease in the concentrations compared to the summer period with a range from 0.02 to 0.6 ppb and an average concentration of about 0.1 ppb. Volatization or displacement of particulate ammonium nitrate by acid from the first filter could have effected the HNO_3 concentrations measured on the second filter.

Measurements of remote sites. Measurements of nitric acid were made by a tandem filter technique in the equatorial Pacific region during late July and early August, 1978 (Huebert, 1980). Nitric acid concentrations ranged between 0.014 and 0.068 ppb and averaged 0.038 ppb. The highest concentrations of nitric acid were observed during rain showers indicating transport from above the boundary layer.

Measurements by a tandem filter technique were collected in an aircraft over a number of remote continental and maritime sites in the Northern and Southern Hemispheres (Huebert and Lazrus, 1978, 1980). Many of the samples contained concentrations of HNO_3 below the detectability limits of 0.01 to 0.03 ppb. Except at mid-altitudes within the boundary layer

in the Northern Hemisphere, measurable concentrations were in the range of 0.1–0.3 ppb. These concentrations were a factor of at least 20 to over 100 less than the average concentrations at urban sites (Table 9). Within the boundary layer at mid-altitudes in the Northern Hemisphere nitric acid concentrations ranged from 0.25 to 0.86 ppb.

Nitric acid as a percentage of ozone concentrations. Nitric acid concentrations vary by a factor of ten as a percentage of ozone concentrations (Table 9). The lower percentages occur at Riverside, CA where nitrate aerosol formation is important and at suburban/rural sites. At the other urban sites nitric acid concentrations range from 5 to 10% of peak O_3 concentrations and 8 to 18% of average O_3 concentrations. At nonurban sites the HNO_3 was a significantly smaller percentage of the O_3 than at urban sites other than Riverside, CA. At all sites the HNO_3 was a larger percentage of the O_3 on a diurnally averaged basis rather than at the time of the O_3 maximum. This result is consistent with the discussion of diurnal variations of HNO_3 relative to O_3 earlier in this section.

4.5. *Hydrogen peroxide*

Atmospheric chemistry. Formation of H_2O_2 can occur through reactions involving HO_2 radicals see references in Section 1). These radicals also react with NO to form NO_2. This competing reaction should inhibit H_2O_2 while NO is being converted to NO_2 particularly within urban areas. No reactions similar to the rapid reactions of O_3 with HNO_3 are known which would remove H_2O_2 from the atmosphere. Therefore, H_2O_2 might be expected to persist overnight.

Methods of measurement. Several chemical methods of analysis are available to analyze H_2O_2 in the ambient atmosphere. The first method used involved the reaction of titanium (IV) sulfate and 8-quinolinol with H_2O_2 to form what may be a peroxidized titanium 8-hydroxyquinolate (Cohen and Purcell, 1967). The titanium (IV) tetrachloride forms a complex with H_2O_2 with an absorption maximum at 410 nm (Pilz and Johann, 1974). A third method in use is based on the chemiluminescent oxidation of luminol by H_2O_2 in the presence of a Cu(II) catalyst in a solution buffered to *pH* 12 (Kok *et al.*, 1978b). The detectability limits were better than 1 ppb.

A difficulty with analytical methods for H_2O_2 which depend on aqueous sampling procedures has been identified (Heikes *et al.*, 1982; Zika and Saltzman, 1982). Both groups of investigators found H_2O_2 to be produced within the aqueous trapping solutions. Zika and Saltzman (1982) attributed the effect to reactions involving gaseous O_3 and its products in aqueous solution leading to H_2O_2 formation. Heikes *et al.*, (1982) attributed the varying yields of H_2O_2 in a series of aqueous trapping solutions not only to positive interference through reactions of O_3 in solution, but also a negative interference by SO_2 in solution.

The detectability limit for H_2O_2 with the long path Fourier transform infrared system is about 40 ppb (Tuazon *et al.*, 1981b). Probably because of the high detectability limit, no H_2O_2 has been reported in the atmosphere by this method.

Ambient air measurements in the United States. The method of Cohen and Purcell (1967) received preliminary evaluation in ambient air measurements made during 1970 in Hoboken, NJ and Riverside, CA (Bufalini *et al.*, 1972). Concentrations of H_2O_2 of up to 40 ppb were measured in Hoboken, NJ and 180 ppb in Riverside, CA. The latter value was obtained during a smog episode when the oxidant concentration was reported as 650 ppb.

Measurements of H_2O_2 were made in July and August 1977 in Claremont, CA and Riverside, CA primarily by use of the chemiluminescent method, but with measurements by the two colorimetric methods described as well (Kok *et al.*, 1978a). The highest concentrations of H_2O_2 measured were 100 ppb on 2 days when the ozone concentration also was 100 ppb and still increasing in concentration. More typically, H_2O_2 concentrations were between 10 and 50 ppb. Direct intercomparisons were made by the three methods on 1 day when the H_2O_2 concentrations were at or below 20 ppb. The H_2O_2 concentrations measured differed by factors of up to 2 or 3 with a lack of consistency among the methods.

Additional measurements of ambient air H_2O_2 concentrations were made in Los Angeles, CA, Claremont, CA and Palo Verdes, CA in the South Coast Air Basin area in 1979 and 1980 (Kok, 1982). At Claremont, CA in June–July, 1979 measurements, typical H_2O_2 concentrations during midday were in the range of 10–15 ppb. Night-time levels of H_2O_2 when O_3 concentrations were below 10 ppb were as high as 5 ppb. However, during an episode on 13–15 September 1979 when the O_3 reached 380 ppb, the H_2O_2 remained in the 1–2 ppb range. In June 1980 at the California State University site in Los Angeles, H_2O_2 concentrations were a few ppb. At a coastal site, Point San Vicente, during 11–12 September 1980, H_2O_2 concentrations in the 5–10 ppb range were observed. Finally, during September–October 1980 in Claremont, CA, despite intense photochemical smog with O_3 concentrations exceeding 400 ppb, H_2O_2 did not exceed 1–2 ppb. Kok (1982) plotted the maximum H_2O_2 concentrations against the maximum O_3 concentrations and found no distinct trends.

Heikes *et al.* (1982) reported H_2O_2 concentrations in each bubbler in a 3 bubbler train to range up to 6 ppb in Minneapolis, MN on one day and 0.5 ppb and less of H_2O_2 in Boulder, CO on another day.

The small amount of H_2O_2 generated by O_3, 1 ppb per 100 ppb, in laboratory experiments (Heikes *et al.*, 1982) is not consistent with H_2O_2 levels when these exceed 5–10 ppb in the South Coast Air Basin. The

high variability in H_2O_2 concentrations on smoggy days over the various measurement periods in the South Coast Air Basin is unexplained. It is not possible at present to adequately evaluate ambient air concentration results for H_2O_2.

Concentration measurements at nonurban sites in the United States. Farmer and Dawson (1982) collected H_2O_2 with water vapor on a cooled surface and analyzed H_2O_2 by luminol chemiluminescence. At a nonurban site 54 km southeast of Tucson, AZ they reported H_2O_2 concentration ranging up to 7 ppb after correcting for consumption of H_2O_2 by reaction with SO_2. In more remote areas near Tucson H_2O_2 concentrations of about 1 ppb were measured.

At a rural site east of Boulder, CO, H_2O_2 concentrations as measured by the luminol chemiluminescent method ranged from 0.2 to 3 ppb during February 1978 (Kelly *et al.*, 1979).

4.6. *Other volatile products of atmospheric photochemical reactions*

Several other volatile chemical products of atmospheric photochemical reactions have been measured in the atmosphere. In general, the measurements available for these products are more limited than for those products discussed earlier in this section.

Nitrous acid. While Tuazon *et al.* (1981a) did not detect *cis*-nitrous acid with an estimated detection limit of 10 ppb, Hanst *et al.* (1982) reported detection of the absorption of HNO_2 near 791 cm^{-1} with a maximum concentration of 5 ppb by LP-FTIR. HNO_2 was detected only in the early morning.

By means of long path differential u.v. absorption spectroscopy, HNO_2 can be detected in the South Coast Air Basin down to 0.28 ppb at 970 m path length using its 354.1 nm absorption band (Platt *et al.*, 1980b). In Riverside, CA and Claremont, CA HNO_2 was measured at night and for several hours after sunrise during 9 days in August and September, 1979 (Platt *et al.*, 1980b). The maximum HNO_2 concentrations measured near sunrise ranged from 1.1 to 4.1 ppb. Because of rapid photolysis in sunlight, HNO_2 concentrations usually decreased down to near detection limits by 0800 to 0900 h. In more recent measurements of HNO_2 in downtown Los Angeles in July 1980, concentrations as high as 8 ppb were obtained just before sunrise (Harris *et al.*, 1982).

Farmer and Dawson (1982) reported measuring HNO_2 after its condensation with water upon a cooled surface by ion chromatography. They observed concentrations in Arizona as high as 0.5 ppb shortly before sunrise, going to low or negligible values after sunrise, consistent with the u.v. measurements discussed above.

In Jülich, West Germany HNO_2 was measured at concentrations from below 0.05 ppb up to 0.8 ppb (Perner and Platt, 1979; Platt and Perner, 1980). The higher concentrations were detected early in the morning. HNO_2 also was measured at Deuselbach, West Germany and at Loop Hand, Ireland (Perner and Platt, 1979; Platt and Perner, 1980). At Deuselbach, a European background site, HNO_2 at the most did not exceed 0.05 to 0.1 ppb. At Loop Hand, Ireland no HNO_2 was detected even in air masses from land areas.

Peroxynitric acid. Peroxynitric acid has been identified in reaction systems in the laboratory (Hanst and Gay, 1977) including the propene–NO_x system (Pitts *et al.*, 1977b). The detectability limit for peroxynitric acid is 8 ppb (Hanst *et al.*, 1982; Tuazon *et al.*, 1981b). It has not been detected at or above 8 ppb in the ambient atmosphere.

Nitrogen trioxide. The radical NO_3 can be formed by the reaction of O_3 with NO_2. NO_3 photolyzes rapidly in sunlight and also reacts rapidly with NO. Therefore, NO_3 is most likely to be detected after sunset, after conversion of NO to NO_2 with significant residue concentrations of NO_2 and O_3 still present in the atmosphere. Measurements for NO_3 have been made by long path differential absorption spectroscopy in Riverside and Claremont, CA during September and October 1979 (Platt *et al.*, 1980a). The strong absorption at 662 and 623 nm were used with a minimum detectable limit of NO_3 at 662 nm corresponding to 0.006 ppb of NO_3 at 970 m path length. The highest concentration measured was 0.355 ppb about 1 h after sunset. On several other days maximum concentrations between 0.1 and 0.3 ppb were measured within 1 to 2 h after sunset. Platt *et al.* (1981) measured significant concentrations of NO_3 at Julüch and Deuselbach, West Germany in 1980. At Deuselbach during a period in April 1980, the NO_3 concentration in early morning reached 0.04 to 0.28 ppb.

Dinitrogen pentoxide. Dinitrogen pentoxide N_2O_5, can be formed through reaction of NO_2 with NO_3 and can react with water to form HNO_3 homogeneously and heterogeneously. However, HNO_3 does not increase in concentration during the night (Tuazon *et al.*, 1981a,b) so there is lack of direct evidence as to the importance of N_2O_5 molecule hydrolysis as a source of HNO_3. A detection limit of 10 ppb by the long path Fourier transform infrared systems used in the South Coast Air Basin area has been estimated (Hanst *et al.*, 1975, 1982). N_2O_5 has not been detected by this method on any of the studies in the South Coast Air Basin (Hanst *et al.*, 1975, 1982; Tuazon *et al.*, 1978, 1980, 1981a,b).

Peroxybenzoyl nitrate. As discussed in Section 2, peroxybenzoyl nitrate is formed and has been measured in laboratory irradiations of benzylic monoalkyl benzenes with NO_x (Appel, 1973; Heuss and Glasson, 1968). An estimate for expected ambient air concentrations of less than 1 ppb has been made based on laboratory yields and ambient air concentrations of benzylic monoalkyl benzenes (Altshuller, 1978). Attempts to measure peroxybenzoyl nitrate in

the ambient atmosphere in the United States have been unsuccessful (Appel, 1973; Hanst *et al.*, 1982). In San Francisco, CA, no peroxybenzoyl nitrate could be detected despite a detectability limit of 0.07 ppb by gas chromotography (Appel, 1973). A detectability limit of 2 ppb for peroxybenzoyl nitrate was estimated by long path Fourier transform infrared spectroscopy, but no peroxybenzoyl nitrate could be detected in Los Angeles, CA (Hanst *et al.*, 1982). Meijer and Neiboer (1976) report measurements of peroxybenzoyl nitrate in an industrial area in The Netherlands.

Alkyl nitrates. Alkyl nitrates have been detected as products in a number of laboratory studies (Section 2). Hanst *et al.* (1982) associated a band at 850 cm^{-1} which appeared in the middle of the day with the possible presence of tertiary nitrates such as *tert*-butyl nitrate.

4.7. *Aerosols*

Atmospheric chemistry. A substantial part of the sulfate, nitrate and organic aerosol measured in the atmosphere can be associated with homogeneous atmospheric photochemical processes. Sulfate, nitrate and some species of organic aerosols can be formed as a result of the reactions of OH radicals with SO_2, NO_2 and higher molecular weight alkenes and alkylbenzenes. Reactions of O_3 with NO_2 can lead to nitrate aerosols at night, particularly in fogs. O_3 can react with higher molecular weight alkenes to form organic aerosols. All of the aerosols formed by such atmospheric processes are sub-μm in size with the possible exception of larger sized hydroscopic aerosols as the result of aerosol growth during periods of high humidities.

Sulfate present in the atmosphere need not be formed exclusively from atmospheric photochemical reactions. Sulfate aerosols in the sub-μm size range in the atmosphere can be produced in combustion processes. Sulfates also can be formed within aqueous aerosols. Oxidation of SO_2 to sulfate in aqueous droplets can be caused by O_3 or H_2O_2 present in the droplet which originated with homogeneous atmospheric photochemical processes and later diffused into the droplets. Some industrial processes contribute larger sized sulfate particles to the atmosphere.

Part of the organic aerosols measured in the atmosphere can have originated in various combustion processes with subsequent emission to the atmosphere. Therefore, it is desirable to be able to differentiate those organic compounds formed by atmospheric photochemical processes.

Atmospheric nitrates also are not uniquely associated with atmospheric photochemical processes. Although ammonium nitrate is formed by reaction of ammonia with nitric acid, the nitrates measured in larger particles are not likely to have been formed by atmospheric photochemical reactions.

Sulfate. In this section measurements of sulfate during the summer are emphasized because the production of sulfate by the photochemical process should be most important during this period. In several studies to be discussed, the authors demonstrate this by obtaining good correlations of sulfate and O_3 concentrations. Primary sulfates have been shown to be significant in the winter, but not in the summer, in parts of the NE United States (Homolya, 1982; Shannon *et al.*, 1980).

Appel *et al.* (1978) measured sulfate concentrations at 2–5-h intervals through a 24-h period at West Covina, CA on 23–24 July 1973 and at Pomona, CA on 16–17 August 1973. Samples were collected on cellulose and cellulose acetate filters. The 24-h average concentrations obtained were 27 $\mu g\ m^{-3}$ at West Covina, CA and 29 $\mu g\ m^{-3}$ at Pomona, CA. The mass median diameters of sulfate obtained were in the 0.3–0.4 μm range, so most of the sulfate was sub-μm in size. O_3 concentrations also were measured.

The sulfate peaked at the same time of the day as the O_3, but the sulfate concentration fell off much less rapidly than the O_3 at night. A positive correlation was obtained between O_3 and a sulfate conversion rate (ratio of particle sulfur less than 0.5 μm to SO_2). Appel *et al.* (1978) attributed an increasing role to photochemical oxidation of SO_2 to sulfate in the eastern part of the basin compared to areas near the ocean in the western part of the basin.

Based on the measurement results provided, the sulfate can be computed as a percentage of the O_3 concentration. At West Covina, CA the sulfate concentration was 9% of the O_3 concentration at the time of maximum O_3 concentration and 13% of the O_3 concentration on a 24-h average basis. At Pomona, CA the sulfate concentration was 8% of the O_3 concentration at the time of maximum O_3 concentration and 27% of the O_3 concentration on a 24-h average basis.

Pitts and Grosjean (1979) measured 24-h average sub-μm sulfate collected on quartz filters along with O_3 at Riverside, CA during 1978. During this period only 1/2 of the sulfate was sub-μm in size. A positive correlation between the sub-μm sulfate and the O_3 concentrations was obtained. Averaging over the entire set of measurements, the sulfate concentration was 4% of the O_3 concentration.

Measurements of sulfate collected on quartz filters and of O_3 are available at a suburban/rural site, Huber Hts., OH, outside of Dayton, OH in July and August 1974 (Spicer *et al.*, 1976). Averaged over the measurement period, the sulfate concentration was 21 $\mu g\ m^{-3}$. The sulfate concentration averaged 22% of the O_3 concentration.

Wolff *et al.* (1979) measured sulfate collected on fluoropore filters along with O_3 at two rural sites in the eastern United States. These rural sites were McKee, KY where measurements were made in July and August 1976 and Keysville, VA where measurements were made in June and July 1976. Averaged over the measurement period, the sulfate concentration at

McKee, KY was 10 $\mu g\ m^{-3}$. At this site, the sulfate concentration at the times of maximum O_3 concentration averaged 6% of the O_3 concentration and on a 24-h average was 9% of the O_3 concentration. Averaged over the measurement period, the sulfate concentration at Keysville, VA was 11 $\mu g\ m^{-3}$. At this site, the sulfate concentration at the time of maximum O_3 concentration averaged 8% of the O_3 concentration and on a 24-h average was 13% of the O_3 concentration.

In most of the studies discussed above, the sulfate concentrations were a significant fraction of the O_3 concentrations, particularly on a 24-h average basis. At several of the South Coast Air Basin sites, the good positive correlations obtained between sulfate and O_3 along with the similarities in diurnal patterns indicates an important if not predominant contribution to sulfate formation from homogeneous atmospheric photochemical reactions.

...rate. Sub-μm ammonium nitrate is formed through homogeneous atmospheric reactions. The formation of ammonium nitrate depends on the atmospheric concentrations of HNO_3 and NH_3 and temperature. Above the relative humidity of deliquescence where solid ammonium nitrate is transformed to an aqueous aerosol, relative humidity and nonidealities in the aqueous aerosol become important. Stelson and Seinfeld (1982a,b) have reviewed previous theoretical and experimental studies and extended the computations for ammonium nitrate in aqueous aerosols. The resulting curves relating the products of partial pressures of HNO_3 and NH_3 to temperature and relative humidity predict that the product of partial pressures will decrease substantially as the relative humidity increases towards 100%. These results have been shown to be in reasonable agreement with available experimental results (Stelson and Seinfeld, 1982a,b).

Several additional complications may enter into determining the partial pressure products. Tang (1980a) has discussed the likelihood that ammonium nitrate aerosols may become hygroscopic at lower relative humidities than bulk materials. Stelson and Seinfeld (1982a,b) assume that the bulk properties of ammonium nitrate can be used. The amounts of unreactive solutes coexisting with ammonium nitrate in aerosols can be significant. Assuming noninteraction with ammonium nitrate, the net effect of such unreactive solutes would be to produce a partial pressure product for HNO_3–NH_3 at a lower relative humidity than for a pure ammonium nitrate–water system. The quantitative effects of solutes including films on the ammonium-nitrate–water system has received little consideration. Tang (1980b) has evaluated the effects of relative humidity and absorption of H_2SO_4 on vaporization of HNO_3 and NH_3 from droplets.

Within the range of meteorological conditions that occur during the warmer months of the year, the theoretical approach of Stelson and Seinfeld (1982a,b) predicts, based on the atmospheric levels of HNO_3 and NH_3 in many areas, that ammonium nitrate should not exist as a solid or liquid aerosol. For example, at 25°C, atmospheric concentrations of 1 ppb for both HNO_3 and NH_3 should not maintain an ammonium nitrate as a solid or liquid aerosol unless the relative humidity exceeded 95%.

Shaw *et al.* (1982) suggest several factors which may lead to ammonium nitrate formation in droplets even when formation is not predicted by the current theoretical treatments. The theoretical treatments assume thermodynamic equilibrium is attained, but this situation may not occur in the ambient atmosphere. Organic films may be formed on the surface of aerosol droplets in the ambient atmosphere which retard volatilization. Such films are not considered in existing theoretical treatments.

A number of experimental studies are available involving particulate nitrate measurements pertinent to present considerations. Several of these studies included O_3 measurements. An estimate of the significance of nitrate concentration levels compared to O_3 concentrations can be made.

Spicer (1977) collected 23-h average particulate matter samples on quartz filters during August and September 1973 in West Covina, CA. The nitrate concentrations measured averaged 1.7 $\mu g\ m^{-3}$ and ranged from 0.3 to 4.0 $\mu g\ m^{-3}$. It was noted that these concentrations were substantially lower than reported in earlier studies in the South Coast Air Basin in which glass fiber filters were used for collection of particulate matter. Laboratory studies were in progress at this time indicating a positive artifact because of its removal of HNO_3 onto glass fiber filters. HNO_3 was not removed by quartz filters. Subsequent laboratory and field studies indicated that a negative nitrate artifact could occur on quartz filters (Appel *et al.*, 1981; Harker *et al.*, 1977). Volatization of ammonium nitrate can occur because of increases in temperature while sampling. Ammonium nitrate also can be displaced off filters by other strong acids.

O_3 concentrations were measured at the West Covina, CA site (Spicer, 1977). The individual daily average particulate nitrate concentrations ranged from 0.3 to 5% of the average daily O_3 concentrations. Averaged over the entire measurement period, the particulate nitrate was 2% of the O_3 concentration. Because of the possibility of a negative nitrate artifact, these percentages probably should be considered minimum values.

In a subsequent study Spicer and Schumacher (1977) reported that the nitrate concentration measured at a site in Upland, CA was strongly dependent on the filter substrate used for collection of particulate matter. Averaged over the measurements made in October and November, 1976, the nitrate concentrations obtained from analyses of nitrate collected on glass fiber filters were 19 times higher than those obtained from analyses of nitrate collected on quartz filters. The average

nitrate concentration obtained on the quartz filters was 1.5 $\mu g\ m^{-3}$ with a range from 0.4 to 3.1 $\mu g\ m^{-3}$. These nitrate concentrations were comparable to those concentrations also obtained on quartz filters earlier at West Covina, CA (Spicer, 1977). However, it is likely that the nitrate concentrations on quartz filters were underestimates of true nitrate concentrations because of negative nitrate artifacts; while the higher concentrations on glass fiber filters were overestimates of true ambient air nitrate concentrations.

Based on comparisons of 24-h average nitrate concentrations on samples collected in Riverside, CA on washed and fired glass fiber filters with those collected on quartz filters placed in tandem, artifact nitrate was estimated (Pitts and Grosjean, 1979). An averaged nitrate artifact of 11% was reported from the samples collected on the glass fiber filters. Higher nitrate concentrations were obtained on quartz filters at Riverside, CA than at West Covina, CA (Spicer, 1977) and Upland, CA (Spicer and Schumacher, 1977). The higher ammonia concentrations in the Riverside, CA area discussed earlier would result in the equilibrium favoring higher ammonium nitrate concentrations.

Pitts and Grosjean (1979) also compared 24-h average sub-μm nitrate measurements obtained from collection of particulate matter on glass fiber filters in 1975 and 1976 and on quartz filters in 1978 with O_3 concentrations. A positive correlation was obtained although there was considerable scatter in individual measurement values. Averaged over all of the measurements, the particulate nitrate concentration was 16 $\mu g\ m^{-3}$ and this nitrate concentration was 15% of the O_3 concentration.

Appel *et al.* (1981) measured inorganic nitrates by the use of two sampling trains. One train consisted of an inert Teflon prefilter followed by a chemically-impregnated or nylon after-filter. This train was designed to collect and measure all of the inorganic nitrate. The second train consisted of a denuder tube used to remove HNO_3 followed by the same filters as in the first train. This second train was designed to measure particulate nitrate. These trains were used to collect samples for analyses of particulate nitrate and HNO_3 at sites in Claremont, CA and Lennox, CA.

The diurnal profiles of particulate nitrate, HNO_3 and O_3 concentrations shown were based on the measurements at Claremont, CA (Appel *et al.*, 1981). The particulate nitrate concentrations tended to peak during daylight at about the same times as the O_3. The diurnal variations in particulate nitrate were not as large as occurred for O_3. Particulate nitrate concentrations exceeded O_3 concentration during several time intervals at night. Averaging over these measurements in July 1979, the particulate nitrate concentration of 24 $\mu g\ m^{-3}$ was 13% of O_3 concentration. At the times the O_3 reached its maximum concentration during the day, the particulate nitrate averaged 6 per cent of the O_3 concentration.

Spicer (1977) collected 23-h average particulate matter samples on quartz filters during July and August 1973 in St. Louis, MO. The nitrate concentrations measured averaged 0.36 $\mu g\ m^{-3}$ and ranged from 0.18 to 0.63 $\mu g\ m^{-3}$. O_3 concentrations were measured also. The individual daily average particulate nitrate concentrations were from 0.2 to 0.8% of the corresponding O_3 concentrations. The overall average particulate nitrate concentration during the study of 0.36 $\mu g\ m^{-3}$ was 0.5% of the overall average O_3 concentration.

In 1974, Spicer *et al.* (1976) collected 24-h average particulate matter samples on quartz filters during July and August at a suburban/rural type site, Huber Hts., OH near Dayton, OH. The nitrate concentrations measured 0.29 $\mu g\ m^{-3}$ and ranged from 0.17 to 0.68 $\mu g\ m^{-3}$. These concentrations were close to those obtained the previous year at the site in St. Louis, MO. Averaged over the period of measurements, the particulate nitrate concentration of 0.29 $\mu g\ m^{-3}$ was 0.4% of the O_3 concentration.

The particulate nitrate concentrations at both of these midwestern sites were low. Some losses of ammonium nitrate off the quartz filters appear likely to have occurred. However, when the observed HNO_3 and NH_3 concentrations are used along with the temperature and relative humidity measurements, the curves prepared by Stelson and Seinfeld (1982a,b) indicated that ammonium nitrate should not have been present. The results in these two studies do not actually provide identification of the presence of ammonium nitrate as the nitrate species present in the finer particle size range. Therefore, the small nitrate concentrations observed may have been associated with a particulate nitrate species other than with ammonium nitrate.

Organic aerosols. The C-containing aerosols formed in atmospheric photochemical reactions should occur as organic aerosols predominately present in the sub-μm size range (Grosjean, 1977). Laboratory experiments indicate that the C_6 and higher molecular weight alkenes, particularly the cyclo-alkenes, and aromatic HCs, are most effective when irradiated with nitrogen oxide in the formation of sub-μm organic aerosols (Altshuller and Bufalini, 1965; Grosjean, 1977). The organic aerosol species identified tend to contain difunctional groups (Grosjean, 1977).

Measurements of the composition of organic aerosols are available from samples collected in the South Coast Air Basin area and elsewhere in California (Appel *et al.*, 1976, 1979; Cronn *et al.*, 1977; Grosjean and Friedlander, 1975; Grosjean *et al.*, 1978; O'Brien, 1975; Schuetzle *et al.*, 1973, 1975).

O'Brien *et al.* (1975) extracted 24-h average samples collected on glass fiber filters with benzene and alcohol. The samples were obtained in the South Coast Air Basin and elsewhere in California. The composition of the extracted materials was identified by use of infrared spectroscopy and paper chromatography. Of the products identified, mono-and dicarboxylic acids and

organic nitrates were those associated with atmospheric photochemical reactions.

Measurements of organic C concentrations and composition were made on samples collected in Pasadena, CA during 6 days in May–October 1973 (Grosjean and Friedlander, 1975). Organic C constituted an appreciable fraction of total particulate matter. Compositional analysis of the organics was obtained by gas chromatography, infrared spectroscopy and a class fractionation technique. During an intense smog, with O_3 concentrations peaking at 670 ppb, organic C concentrations were very high. The organic carbon concentrations obtained during the afternoon hours of this smog episode showed good correlation with the O_3 concentrations.

Grosjean *et al.* (1978) identified 15 aliphatic dicarboxylic acids ranging from malonic acid to sebacic acid by combined gas chromatography–mass spectrometry in samples collected in Riverside, CA. These investigators attributed these products to atmospheric photochemical reactions rather than primary emissions.

Schuetzle *et al.* (1973) reported on the use of high resolution mass spectrometry to identify a large number of organic and inorganic compounds in atmospheric aerosols. In a subsequent investigation of samples collected in Pasadena, CA on 21–23 September 1972, a large number of organic species were identified and quantitated on particle-sized samples (Schuetzle *et al.*, 1975). The secondary organic aerosols were predominately in the sub-μm fraction and displayed a rapid rise and fall in concentration during the day. The primary aerosol showed a less distinctive diurnal pattern. The aliphatic compounds with difunctional groups included dicarboxylic acids, as well as compounds with the following difunctional groups: acid/alcohol, acid/aldehyde, acid/nitrate or nitrate, aldehyde/nitrate, aldehyde/alcohol, and dialdehydes. Several secondary aromatic compounds also were identified. At the peak in secondary aerosol formation, all of these compounds summed to 21 $\mu g\ m^{-3}$.

These same techniques were applied to samples collected for 2-h intervals at West Covina, CA during a smog episode on 24 July 1973 (Cronn *et al.*, 1977). At the time of maximum O_3 concentration, the concentration of secondary organic C compounds measured, summed to about 30 $\mu g\ m^{-3}$. A high correlation between O_3 concentrations and most of the secondary organic aerosols was obtained. At the peak O_3 concentration of near 1000 $\mu g\ m^{-3}$, the secondary organic C concentration was 3% of the O_3 concentration.

Appel *et al.* (1976, 1979) estimated the amounts of elemental, primary and secondary C-containing aerosols in particulate matter below 3.5 μm in size by use of multiple organic extractions. Extraction of particulate matter with cyclohexane were followed by extraction with benzene and finally with methanol/chloroform. The C-containing particulate matter extracted with cyclohexane was considered as of primary origin because of the low polarity of most of the compounds in the primary fraction. Additional evidence for the material in the cyclohexane extracts being of primary origin was the similarity of composition of this fraction to that of auto exhaust aerosols. Samples were collected on glass fiber filters during several days in July–October 1973 at four locations from west to east across the South Coast Air Basin (Appel *et al.*, 1976). The average composition was elemental carbon, 22% (an upper limit), primary organic carbon, 28% and secondary organic carbon, 50%. The secondary organic carbon varied from 24 to 76% of the C-containing particulate matter below 3.5 μm. The secondary organic C showed a high correlation with the mean O_3 concentration between 0800 and 1600 h, while the primary organic C showed a poor correlation.

In subsequent work, the same extraction technique was applied to samples collected on 9–12 July 1975 at three sites in the South Coast Air Basin (Appel *et al.*, 1979). The average composition was elemental C, 43%, primary organic C, 17% and secondary organic C, 40%. In this later study, high resolution mass spectroscopy also was utilized. While the mass spectromatic results provided general confirmation that cyclohexane extraction did remove primary type compounds (alkanes, alkenes and alkybenzenes) some hexanedioic acid and smaller amounts of some of the other secondary aerosol compounds also were extracted. Using the 2-h average analyses of secondary organic aerosol along with the O_3 measurements for 9 and 10 July 1975 at Pasadena, CA and Pomona, CA, the percentages the secondary organic aerosol concentrations constituted the O_3 measurements can be calculated. The percentages averaged over the entire 14-h measurement period are as follows: Pasadena, CA, 9 and 10 July, 3 and 5; Pomona, CA, 9 and 10 July, 6 and 7. The percentages at the maximum O_3 concentration were as follows: Pasadena, CA, 9 and 10 July, 4 and 4; Pomona, CA, 9 and 10 July, 3 and 6.

The percentages secondary organic aerosols constitute of O_3 concentrations based on the results from the work of Cronn *et al.* (1977) and Appel *et al.* (1979) usually are smaller than that contributed by sulfate and nitrate in the South Coast Air Basin. Similar detailed compositional studies of organic aerosols are not available for sites elsewhere in the United States.

5. GENERAL DISCUSSION

Most of the photochemically generated reaction products identified in laboratory studies also have been identified in the ambient atmosphere. These products as discussed in Section 4 include the following substances: formaldehyde, acetaldehyde, propanal, *n*-butanal, acrolein, benzaldehyde, 2-butanone, formic acid, peroxyacetyl nitrate, peroxypropionyl nitrate, peroxybenzoyl nitrate, nitric acid, nitrous acid, nitrogen trioxide, hydrogen peroxide, and the sulfate,

nitrate and organic carbon compounds in sub-μm aerosols. Some of these products have been identified by a single investigator at one site, while other products have been measured consistently at urban and nonurban locations in the United States, Europe, Japan and/or other areas of the world. The more abundant products which have been widely measured include formaldehyde, PAN, HNO_3 and sulfate.

The largest group of measurements are available within the South Coast Air Basin of California. In the South Coast Air Basin the concentration of products including ozone are usually higher than in other urban areas. However, the concentrations of several of the more abundant products in other urban areas will overlap those in the South Coast Air Basin. Concentrations of formaldehyde, PAN and HNO_3 have been measured in nonurban locations in the United States, Europe and elsewhere and tend to be significantly lower than within urban areas.

At remote sites where clean maritime air is sampled, formaldehyde and HNO_3 are usually reported at concentration levels from a factor of 10 to 100 lower than the concentrations measured within urban areas. The concentrations of PANs measured at remote locations do not appear to be as low as those of formaldehyde and HNO_3 relative to the corresponding concentrations within urban areas. This latter result may be associated with PAN being ubiquitous in the troposphere (Singh and Hanst, 1981; Spicer *et al.*, 1983). The oxidation of the long-lived ethane and propane molecules are considered to be sources for the tropospheric background of PAN (Singh and Hanst, 1981).

5.1. *Atmospheric loadings of other products and their relationship to O_3*

Based on the ambient air measurements discussed in Section 4 the following statements can be made: (1) the concentrations of O_3 measured substantially exceeds the concentrations of most other individual products of atmospheric photochemical reactions formed concurrently. This is especially so at the time that O_3 is at its maximum concentration during the day. (2) The concentrations of the other products relative to the concentrations of O_3 can vary substantially from site to site within the same urban area as well as among urban areas and (3) The sum of concentrations of other products can be substantial compared to O_3 concentrations in at least certain areas of the United States.

The third of the statements above requires additional consideration. To do this a quantitative synthesis of the measurements of individual products is necessary. The one technique providing concurrent measurements of O_3 and of several other products is long path Fourier transform infrared spectroscopy, LP-FTIR, as utilized at several sites in the South Coast Air Basin areas.

20 days have been selected from the LP-FTIR measurements as useable in terms of completeness and duration of the measurements. The specific days were selected from the measurements in Riverside, CA, (University of California, Riverside) in 1976 (Tuazon *et al.*, 1978) and in 1977 (Tuazon *et al.*, 1980), in Claremont, CA (Harvey Mudd College) in 1978) (Tuazon *et al.*, 1981a) and in 1979 (Tuazon *et al.*, 1981b) and Los Angeles, CA (California State University) in 1980 (Hanst *et al.*, 1982). The computations based on these measurements are summarized in Table 10. The percentages that the concentrations of formaldehyde, PAN, formic acid and HNO_3 individually and their sums are of the O_3 concentrations are given (a) at the times the O_3 reaches its maximum concentration each day, (b) averaged over the entire measurement interval each day. Concentration values below detectability limits do occur for one or more products during many of the 20 days. To evaluate the significance of the uncertainities resulting, it was assumed that these missing concentration values either could equal 0 ppb or could equal a concentration just below the detectability limit, i.e. if detectability limit was 6 ppb, concentration was assumed to be 5 ppb. Formic acid was not reported at the Claremont, CA site during the 1979 measurements. Formic acid averaged about 0.2 of the formaldehyde concentration when formic acid was measured in the other LP-FTIR studies. It is assumed that the missing formic acid concentration in the 1979 study could equal either 0 ppb or 0.2 × HCHO. With one exception, the percentages given in the last column for the (sum of products/O_3) × 100 show only a small uncertainty results from the missing values.

As shown at the bottom of Table 10, averaging over the 20 days of measurement the sum of the concentrations of the four other products is 25% of the O_3 concentration at the time of maximum O_3 concentration, but is over 33% of the O_3 concentration averaging over the entire time intervals of measurement. This effect of averaging time on this relationship is better demonstrated if the measurements are divided into two groups. The 11 days during which the measurement intervals range from 4–8 h constitute one group, while the 9 days the measurement intervals range from 10 to 23 h constitute the other group of results.

Averaging over the 9 days, the sum of the percentages for the other four products are 30% of the O_3 at the time of maximum O_3 concentration and 57% of the O_3 concentration averaging over measurement intervals. Averaging over the 11 days, the sum of the percentages for the four other products are 19% of the O_3 at the time of maximum O_3 concentration and 20% of the O_3 concentration averaging over measurement intervals. When measurements are available permitting averaging over substantial portions of 24-h periods, the sum of the other products account for about twice the percentage of the O_3 concentration than they do during the several hours when O_3 is at or near its maximum concentration. Much of the effect of averaging time is a result of the diurnal characteristics of formaldehyde. Averaging over the 9 days with the

Table 10. Other products measured in LP-FTIR studies as a percentage of the concentration of ozone

Site (Reference)	Date	Measurement intervals, PDS	Concentration of O_3 (ppb)		Percentage of other products of ozone, (a) at O_3 peak, (b) on average								(Sum of products/O_3) × 100 O_3 peak average	
					HCHO		PAN		HCOOH		HNO_3			
			a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Riverside, CA	15/10/76	1552–1947	285	199	4	6	5	5	1	2	0–2*	1–3*	10–12	14–16
(Tuazon *et al.*,	21/07/77	1140–1857	264	209	7	8	4	3	2	2	4	1–3*	17	14–16
1978, 1980)	25/07/77	1058–1755	291	179	7	8	3	2	1	1	7	6	18	17
	10/08/77	1333–1837	234	179	6	8	4	4	3	3	0–2*	0–3*	13–15	15–18
	11/08/77	1157–1737	287	211	9	10	5	3	3	3	4	4	21	20
	12/08/77	1200–1749	249	197	9	10	4	4	3	4	4	5	20	23
	04/10/77	1135–1705	195	156	11	12	4	3	4	3	8	5–6*	27	23–24
	11/10/77	1305–1910	242	168	11	14	7	5	3	4	0–2*	1–3*	21–23	24–26
	14/10/77	1205–1910	260	172	8	13	4	5	3	3	3	2–4*	18	23–25
	17/10/77	1302–1900	240	170	10	12	5	4	4	4	0–2*	1–3*	19–21	21–23
Claremont, CA	09/10/78	1000–2100	163	55–57†	10	30	4	2–4†	1	5	10	23	25	60–62
(Tuazon *et al.*,	10/10/78	1000–2000	227	64–66†	13	28	6	3–5‡	1	3	12	20	32	54–56
1981a, 1981b)	11/10/78	0900–2000	280	97	11	25	5	4	2	3	11	16	29	48
	12/10/78	1000–2375	360	135	14	26	6	7	4	5	9	14	33	52
	13/10/78	0007–2335	454	91–95†	16	39	8	11	4	9	11	18–19*	39	77–78
	27/08/79	0600–1730	210	125	5	10	3	5	0–1§	0–2§	7	8–10*	15–16	23–27
	28/08/79	0000–1633	101	33	15	15–21*	4	6	0–3§	0–3§	10	6–18*	29–32	27–48
	02/09/79	1310–1931	230	161	9	12	4	4	0–2§	0–2§	4	4	17–19	20–22
Los Angeles, CA	26/06/80	0635–1945	272	97	18	36	6	7	4	4	4	6	32	53
(Hanst *et al.*,	27/06/80	0045–1335	202	62	24	71	5	11	3	6	6	13	38	101
1982)		Averages			11	20	5	5	2–3	3–4	6	8–9	24–25	36–38

* Some concentration values for nitric acid below detectability limit of 6 ppb, computations made assuming missing values to be either 0 or 5 ppb.
† Some concentration values for ozone below detectability limit of 10 ppb, computations made assuming missing values to be either 0 or 9 ppb.
‡ Some concentration values for PAN below detectability limit of 3 ppb, computations made assuming missing values to be either 0 or 2 ppb.
§ Formic acid concentrations not measured, computations made assuming missing values to be either 0 or 0.2 × HCHO concentrations.

longer measurement intervals, the formaldehyde concentration was 14% of the O_3 at the time O_3 peaked in concentration, while the formaldehyde concentration increased to 31% of the ozone concentration averaging over the measurement intervals.

Substantial variability occurs in the concentrations and the percentages of the other products relative to O_3 from day to day at a site. Even larger variations can occur between sites with the largest differences between the measurements on 15 October 1976 at Riverside, CA and on 27 June 1980 in Los Angeles, CA. At the time of maximum O_3 concentration, the percentages the other four products are of the O_3 concentration tend to be substantially higher at the sites in Claremont, CA and in Los Angeles, CA than the site at Riverside, CA. This difference among sites results from the formaldehyde and/or HNO_3 concentrations being substantially higher on an absolute basis as well as relative to O_3 at the sites in Claremont, CA and Los Angeles, CA than in Riverside, CA.

Other measurements made in the South Coast Air Basin area not involving the LP-FTIR technique indicate the presence of substantial concentrations of additional photochemically generated products. Two examples are aldehydes other than formaldehyde and a number of the aerosol species in the atmosphere.

The sum of the aldehydes other than formaldehyde measured at sites in the western part of the South Coast Air Basin area just about equal the concentration of formaldehyde measured. A number of studies made during the 1950s and 1960s provided measurements of the concentrations of total aldehydes. A recent study in Claremont, CA in 1980 also gave an average concentration for the sum of other aldehydes measured almost equaling the formaldehyde concentration. If this same relationship can be applied during the LP-FTIR measurements, an incremental percentage equal to the formaldehyde concentration would be added to the percentages in Table 10. This would increase the average percentages at the time of maximum O_3 concentration up to 35% and the percentages averaged over the measurement intervals to 57%. For the 9 days with the longer measurement intervals the corresponding percentages would be increased to 44 and 88%.

The sub-μm aerosol concentration of sulfate, nitrate and organic aerosols generated by photochemical processes also can be significant compared to the ozone concentration. With a few exceptions, measurements of aerosols are available on a 24-h average basis so diurnal variations cannot be compared with those of O_3 or other products. The South Coast Air Basin area measurements of aerosol in terms of 24-h average percentages of aerosols compared to O_3 concentrations can be summarized as follows: sulfate, 4–27%; nitrate, 2–15%; secondary organic aerosols, 4–6%. Summing these percentages results in minimum, maximum and mid-range percentages of 10, 48 and 29%. Again, as for aldehydes other than formaldehyde, a substantial percentage contribution of photochemically generated aerosols to the atmospheric loadings of products is indicated.

Other species including PANs other than PAN, other organic nitrates, and H_2O_2 also will contribute to the atmospheric loadings relative to O_3. However, the concentration levels of these other products appear to be in the ppt to the low ppb range. Therefore, their contributions on a percentage basis relative to O_3 appears to be small.

Less complete measurements are available at other geographical locations. There is very little overlap in the measurements. For example, while both aldehydes and PAN have been measure in Houston, TX, the measurements were not made at the same sites or during the same periods of time (Tables 5 and 6). Aldehyde concentrations at sites in Houston, TX, Columbus, OH and Atlanta, GA during daylight ranged from 30 to 170% of the O_3/oxidant concentrations during the same time intervals. Peroxyacyl nitrate concentrations at urban sites in Houston, TX, St. Louis, MO, Dayton, OH and Hoboken, NJ during 8- to 24-h diurnal periods ranged from 2 to 15% of the O_3/oxidant concentrations (Table 6). Averaging over these sites, the PAN was 5% of the O_3/oxidant concentration. HNO_3 concentrations at urban sites in St. Louis, MO and Houston, TX were 9 and 18% of O_3/oxidant concentrations on a 23-h average basis. Therefore, the sum of aldehydes, PAN and HNO_3 concentrations based on these results come close to equaling the O_3 concentration on a 24-h average basis. Sufficient measurements at the time of maximum O_3/oxidant concentration are not available to make an estimate of how the sum of products compares to O_3 at the time of maximum O_3 concentration.

The results above indicate substantial atmospheric loadings of other products of atmospheric photochemical reactions occuring in the South Coast Air Basin and in urban areas elsewhere in the United States. The limited measurements of formaldehyde, PAN and HNO_3 in residential/suburban or nonurban or remote sites in the United States, Europe, Japan and elsewhere indicate these other products as substantially less significant relative to O_3 than at urban sites. Therefore, any potential concern as to these products probably should be focused within urban areas.

5.2. *Effects of variations of hydrocarbon and/or nitrogen oxide concentration on yields of products*

Three studies were utilized in Sections 2.2 and 2.3 to evaluate the effects of changes in the initial concentration levels of HCs and/or NO_x on product yields of O_3, formaldehyde and PAN. The results of these studies could be expressed in terms of concentrations of products and/or dosages, ppm × time, of products, The directional changes of the product concentrations or dosages with reductions in reactants are summarized in Table 11. The three products consistently decrease in concentration and in dosages when the initial HC concentrations are reduced in the three studies. In contrast, reductions in NO_x causes no

Table 11. Changes in concentrations or dosages of products with reductions in concentrations of reactants

Study	Product	Yield	Ratio(s)	Directional changes in product yields: reduce HC	reduce NO_x	reduce HC and NO_x
Pitts *et al.* (1979)	ozone	concn	10:1 to	decrease	unchanged	decrease
		dosage	95:1	decrease	increase	decrease
	PAN	concn		decrease	small decrease	decrease
		dosage		decrease	increase	decrease
	CH_2O	concn		decrease	unchanged	decrease
		dosage		decrease	increase	decrease
Leach *et al.* (1964)	oxidant	concn	3:1 to	decrease	increase	decrease (12:1);
Korth *et al.* (1964)	CH_2O	concn	12:1			increase (6:1)
Dimitriades (1970)	oxidant	dosage	1:1 to 12:1	decrease	increase	decreased at ratios above 3.6:1; increased at lower ratios
	PAN	dosage		decrease	increase	decreased at ratios above 2.4:1; increased at lower ratios
	CH_2O	dosage		decrease	increase	decreased

consistent trend in the concentration of products, but increases the dosages of products. Concurrent reduction of HC and NO_x result in decreases in both concentration and dosage of products at higher ratios of reactants. At lower ratios of reactants, reduction in HC and in NO_x increases the dosages of oxidant and PAN, but not formaldehyde. Quantitatively, as discussed in Section 2.3, the percentage changes in the three products are usually different. These results also imply that other products not measured may have significantly different behavior than the three products considered.

Another approach is to consider the relative relationship between the ambient air concentrations of products. It is useful to consider the same LP-FTIR measurements discussed in Section 4. The measurements of the maximum diurnal O_3 concentrations have been plotted relative to the concentrations at the same times of each of the other products measured. The conclusions obtained from examining these plots are as follows:

(1) The concentrations of other products show the same directional characteristics as the O_3 concentration.

(2) These relationships are not linear. Significant curvatures are apparent in the plots, particularly at the higher concentrations measured. Corresponding to a 50% reduction in the concentration of O_3 from its highest measured diurnal maximum concentration, the concentrations of the other products decreased by more than 50%.

(3) There is a considerable scatter in the measurement values of each of the other products at a particular O_3 concentration. For example in the 270–280 ppb range of concentration for O_3, the formaldehyde concentrations range from 12 to 31 ppb.

(4) The scatter in measurement values is not random. Based on the O_3–formaldehyde plot in the 200–300 ppb O_3 range, the lowest concentration values of formaldehyde were reported at Riverside, CA in 1976 while those in Claremont, CA in 1978 are consistently high, with the results of the other two studies at these locations falling in between these studies. Similar site specific effects can be identified in the other plots.

(5) The amount of scatter varied from plot to plot. The results for the O_3–PAN plot show the least scatter. The variability observed is likely to be due to a combination of factors including differing effects of transport, varying contributions of local primary emissions of products to the total loading of products, and differences in precursor emission densities.

These ambient air results suggest, that at least in the South Coast Air Basin O_3 serves as a surrogate directionally for other products. Adequate measurements are not available in other geographical areas relating O_3 to a number of other products.

5.3. *Effects of variations in hydrocarbon composition on yields of products*

The results of Dimitriades *et al.* (1973) and of Pitts *et al.* (1979) have been used to examine the effects of compositional changes in HCs on irradiation product yields. Variation in the composition of gasolines over a wide range results in about several fold changes in the percentages other irradiation product concentrations are of oxidant concentrations. PANs were more sensitive to changes in gasoline composition than is formaldehyde. The composition changes made in the experiments of Pitts *et al.* (1979) resulted in different percentage changes in formaldehyde concentrations and dosages than in PAN dosages. Increasing the percentage of unsaturated HC in the HC mixtures results in increasing yields of all of the products

measured. The percentages the products were of the O_3 concentrations in these laboratory studies fell within the range of percentages observed in the ambient air studies.

6. SUMMARY AND CONCLUSIONS

(1) A number of the products identified as significant in laboratory smog chamber studies have been identified and measured in the ambient atmosphere. Such results indicate that results of smog chamber studies can provide substantial guidance to ambient air measurement programs.

(2) Carbon balances obtained from smog chamber studies can be poor, especially in mixtures with high initial aromatic HC concentration levels. Such results suggest that significant amounts of organic products remain to be identified and quantitated in the ambient air.

(3) Varying the HC composition in laboratory studies shows that the effects of such variations effect the individual products differently.

(4) Individual products of atmospheric photochemical reactions, other than NO_2, usually occur at concentrations 1–10% that of O_3 in ambient air. However, a class of compounds such as the aldehydes, have been reported to occur at concentrations approaching or even exceeding O_3 concentrations.

(5) A number of the other products of atmospheric photochemical reactions measured in the ambient air do not peak as sharply as does O_3. These products do not decrease as rapidly in concentration as does O_3 in the evenings and at night. In particular, formaldehyde and other aldehydes show much flatter diurnal profiles than O_3. As a result, aldehydes and other products are more significant relative to O_3 over longer averaging intervals. For example, the sum of the formaldehyde, PAN, formic acid and HNO_3 obtained from LP-FTIR studies can be about twice the percentage of the O_3 concentrations on a 24-h basis that they are at the time of maximum O_3 concentration.

(6) It is estimated that the volatile products and the aerosols produced by atmospheric photochemical reactions measured within the South Coast Air Basin area, when summed, can equal about half the O_3 concentration at the time of maximum O_3 concentration. These summed products can equal or exceed the O_3 concentrations when averaged over the daylight hours or over 24 h in some parts of the South Coast Air Basin and in other urban areas.

(7) Measurements of formaldehyde, PANs, nitric acid and sulfates are available at a number of rural and remote sites. With the exception of sulfate, the concentrations of these products occur as very low percentages of O_3 concentrations in such areas.

(8) Within a geographical area such as the South Coast Air Basin, there can be several fold or even greater variations in the percentage of other products to O_3 from site to site.

(9) Trends in formaldehyde and PAN concentrations can be evaluated within the South Coast Air Basin area. However, lack of fully consistent measurements is a limiting factor. Annual average PAN concentrations do not vary significantly between 1967 at a site in Riverside, CA. However, other measurements suggest a possible downward trend in PAN in the western part of the South Coast Air Basin. A moderate downward trend in formaldehyde concentrations may have occurred within the South Coast Air Basin between the 1960s and late 1970s.

(10) O_3, formaldehyde and PAN show the same directional trends over short time periods in ambient air. When only the effects of changes in precursor concentrations are isolated in the laboratory, these products do not always show the same directional characteristics. Even when the directional characteristics are the same, both laboratory and ambient air results show each product often shows unique quantitative variations.

Disclaimer—Policy issues discussed and implied in this paper should not be construed to represent official Agency policy. Furthermore, mention of trade names or of commercial products does not constitute endorsement or recommendation for use.

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